PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

In the Application of:

JING C. CHANG ET AL. CASE NO.: SO0007 US NA

APPLICATION NO.: 10/733,998 GROUP ART UNIT: 1732

FILED: DECEMBER 10, 2003 EXAMINER: L.B. TENTONI

FOR: PROCESSES OF MAKING STAPLE FIBERS (AMENDED)

Commissioner for Patents
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APPELLANTS' BRIEF ON APPEAL

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TABLE OF AUTHORITIES

I. INTRODUCTION

This is an appeal from the final rejection of claims 1-30 entered in the Final Office Action dated 6 November 2006.

A Notice of Appeal against the final rejections was filed 7 February 2007. As a consequence, a Petition for an Extension of Time under 37 C.F.R. §1.136, requesting a two (2) month extension of time, is also enclosed.

II. REAL PARTY IN INTEREST

The real party in interest is E. I. du Pont de Nemours and Company (Wilmington, DE).

III. RELATED APPEALS OR INTERFERENCES

It is believed that there are no related appeals or interferences that will directly affect or be directly affected by or have a bearing on the Board's decision in this pending appeal.

IV. STATUS OF THE CLAIMS

This application was originally filed with claims 1-45, directed to a first process for producing a 6-25 dpf carpet staple fiber (claims 1-15); a second process for producing a 1–6 dpf textile staple fiber (claims 16-30); various fibers produced by the aforementioned processes (claims 31-37 and 44-45); and various products made with such fibers (claims 38-43).

In a First Office Action dated 8 June 2006, a restriction requirement was entered requiring the Appellants to elect between the process claims (Group 1, claims 1-30) and the fiber and fiber article claims (Group 2, claims 31-43). In this First Office Action, the title of the application was objected to, and claims 1-30 were also rejected on prior art grounds.

In an "Amendment and Response" dated 29 August 2006, the Appellants elected to prosecute the Group 1 claims, and canceled the Group 2 claims without prejudice on any sort. The Appellants further amended the title of the application to its current form, as well as

claims 1, 6, 7, 15, 16, 22, 23 and 30, and responded to the rejections of record.

In the aforementioned Final Office Action dated 6 November 2006, one rejection was withdrawn but the rejections currently on appeal were maintained against all of claims 1-30.

The Appellants filed a "Response After Final Rejection" dated 5 December 2006, but the rejections of record were again maintained in an Advisory Action mailed 8 January 2007.

The claims remaining in this application and involved in the present appeal are thus claims 1-30. A clean copy of all claims in this application (including their status) is attached hereto as Appendix A.

V. STATUS OF AMENDMENTS

No amendment to the claims was filed subsequent to the Final Rejection, and no amendment remains outstanding.

VI. SUMMARY OF THE CLAIMED SUBJECT MATTER

The present application is directed generally to processes for preparing two different types of staple fiber from poly(trimethylene terephthalate) ("PTT"):

finer textile staple fibers of 1-6 dpf (claims 16-30), and

thicker carpet staple fibers of 6-25 dpf (claims 1-15).

The invention is, on a broad basis (paraphrased), a process for producing either a 6-25 dpf carpet staple fiber (original claim 1, and lines 17-20 on page 4), or a 1-6 dpf textile staple fiber (original claim 16, and lines 17-20 on page 4), comprising the following steps:

(1) melt spinning a PTT fiber (line 24-25 on page 11);

(2) **accumulating the melt spun fibers under conditions so as to result in an aged undrawn yarn** (lines 16-27 on page 7, and "1" in Fig. 1);

(3) prewetting the undrawn aged PTT yarn at a temperature of less than about 45°C (lines 24-30 on page 11, and "2" in Fig. 1);

(4) drawing the prewetted PTT yarn **under wet conditions** at a temperature of from about 45°C to about 95°C in a first stage to a length of about 30 to about 90 percent of its final length (lines 1-28 on page 12, and "9" in Fig. 1);

(3) further drawing the partially drawn PTT yarn in a second stage at a temperature from about 45°C to about 98°C **under wet conditions** (lines 5-14 on page 13, and "18-21" in Fig. 1);

(4) crimping the drawn yarn (lines 16-28 on page 15, and "27" in Fig. 1);

(5) thermo-fixing the crimped yarn in the presence of steam at a temperature from about 80°C to about 100°C (lines 6-10 on page 16, and "28" in Fig. 1); and

(6) drying the crimped yarn at 60°C to 140°C (lines 11-17 on page 16, and "29" in Fig. 1).

Preferred claimed embodiments applicable to both processes include:

(i) both the prewetting and drawing being carried out under water or under an aqueous solution of processing finish (lines 20-24 on page 12);

(ii) the first draw stage being carried out at a temperature of about 80°C or less, more preferably about 70°C or less, still more preferably about 60°C or less, and still more preferably about 50°C to about 55°C (lines 2-7 on page 12);

(iii) the second draw stage being carrier out at a temperature of about 60°C to about 80°C (lines 9-11 on page 13);

(iv) the thermofixing being carried out at a temperature of about 85°C (original claims 13 and 29); and

(v) the crimped yarn being dried at a temperature of from about 60°C to about 100°C (lines 13-16 on page 16).

Preferred claimed embodiments specific to the process for producing carpet staple fibers include:

(i) the undrawn yarn being spun on equipment having a spinneret capillary density of at least 2/cm^2 and a quench zone shorter than about 16 feet (paragraph bridging pages 14-15 and lines 10-11 on page 15);

(ii) the undrawn yarn being spun at a speed less than about 600 ypm (lines 25-28 on page 14);

(iii) during the prewetting and drawing, the yarn being in the form of a spun rope of less than about 300,000 denier/inch (lines 29-32 on page 12);

(iv) in said first draw stage, the yarn being drawn to a length from about 40 to about 70 percent, more preferably from about 50 to about 55 percent, of its final length (lines 11-18 on page 12); and

(v) the drawn yarn having a denier of 6 to 20 dpf (original claim 14).

Preferred claimed embodiments specific to the process for producing textile staple fibers include:

(i) the undrawn yarn being spun on equipment having a spinneret capillary density of at least 8/cm^2 and a quench zone shorter than about 16 feet (paragraph bridging pages 14-15 and lines 10-11 on page 15);

(ii) the undrawn yarn being spun at a speed of 1300 ypm or less, and more preferably 900 ypm or less (original claims 18 and 19);

(iii) during the prewetting and drawing, the yarn being in the form of a spun rope of less than about 200,000 denier/inch (lines 29-32 on page 12); and

(iv) in said first draw stage, the yarn being drawn to a length from about 40 to about 90 percent, more preferably from about 70 to about 90 percent, of its final length (lines 11-18 on page 12).

As discussed throughout the present application, the problem addressed by the invention is how to overcome processing problems **on a commercial scale** when drawing **aged undrawn** PTT fibers (see. e.g., lines 18-28 on page 2, and lines 16-27 on page 7, of the specification). Commercial scale PTT processes normally result in aged PTT fibers because of the processing time to collect sufficient tow cans (see "1" in Fig. 1) of PTT fiber for running through the drawing steps. Aging causes the PTT fibers to shrink and become brittle.

There are known ways to address this shrinking (aging) issue. For example, instead of ultimately collecting the spun PTT in tow cans, it is known to collect the fibers on takeup reels or similar devices, and to feed the so-collected PTT fibers directly into the drawing process. In this case the fibers are maintained in an effectively tensioned state, thus not allowed to significantly relax (and shrink), and thus **would not be aged undrawn yarn within the meaning of the present invention**. While useful, this means for controlling the problem is not practical at commercial spinning speeds and under other commercial conditions.

Additional measures to control the shrinkage and aging are disclosed, for example, in Casey et al (WO01/68962 discussed in detail below), which describes cooling the spun fibers at some point (e.g., during the quenching process) prior to collection on takeup reels (under tension), then preferably maintaining the collected fibers in a cooled, climate controlled room (see, e.g., the disclosure in Casey et al at lines 11-18 on page 3, and line 26 on page 10 though line 10 on page 11). Prior to removing the fibers from the cooled conditions, Casey et al recommends to make sure the undrawn yarn is under uniform roll tension, with preconditioning prior to drawing occurring under tension as well. Again, the predrawn yarns treated as in Casey et al **would not be aged undrawn yarn within the meaning of the present invention**.

While the process as disclosed in Casey et al is useful, all of the additional conditions for controlling the aging problem are not practical at commercial spinning speeds and under other commercial conditions.

Casey et al does indicated (lines 7-10 on page 11) that, "[e]ven if the PTT UDY shrinks it is possible to convert this UDY into a first grade commercial staple product during draw processing with minor impact on product quality". Casey et al, however, does not appear to teach specifically how to convert the shrunken (aged) PTT undrawn yarn into first grade product. In other words, Casey et al does not disclose what process conditions are necessary to control/adjust in order to draw aged undrawn PTT yarn. **That is exactly the problem being addressed by the present invention!**

VII. GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

A. 35 U.S.C. §102(b) - are claims 16-30 anticipated by the disclosure of Casey et al (WO01/68962)?

B. 35 U.S.C. §103(a) - are claims 16-30 unpatentable over the disclosure of Casey et al.?

C. 35 U.S.C. §103(a) - are claims 1-15 unpatentable over the disclosure of Casey et al, as applied to claims 16-30, and further in view of Hernandez et al (US2002/0071951A1)?

VIII. ARGUMENT

A. ANTICIPATION REJECTION

As just indicated, one of the grounds to be reviewed on appeal relates to the rejection of claims 16-30 as allegedly anticipated by the disclosure of Casey et al. The Appellants respectfully traverse this rejection.

The invention of claims 16-30 is, on a broad basis (paraphrased), a process for producing a 1-6 dpf textile staple fiber comprising the following steps:

(1) melt spinning a PTT fiber;

(2) **accumulating the melt spun fibers under conditions so as to result in an aged undrawn yarn;**

(3) prewetting the undrawn aged PTT yarn at a temperature of less than about 45°C;

(4) drawing the prewetted PTT yarn **under wet conditions** at a temperature of from about 45°C to about 95°C in a first stage to a length of about 30 to about 90 percent of its final length;

(3) further drawing the partially drawn PTT yarn in a second stage at a temperature from about 45°C to about 98°C **under wet conditions**;

(4) crimping the drawn yarn;

(5) thermo-fixing the crimped yarn in the presence of steam at a temperature from about 80°C to about 100°C; and

(6) drying the crimped yarn at 60°C to 140°C.

The present invention, **when considered as a whole**, provides a combination of process conditions and steps that the Applicants have found effective to solve the problem identified above. Admittedly, Casey et al generally discloses a number of these conditions and steps, but it is the claimed combination and totality of these conditions, steps and circumstances which must be evaluated for patentability.

It is well established that anticipation requires the disclosure in a single prior art reference of each and every element of a claimed invention arranged as set forth in the claim. See, *e.g.*, Connell et al. v. Sears, Roebuck & Co., 220 U.S.P.Q. 193, 198 (Fed. Cir. 1983). It is thus not sufficient for anticipation purposes for a prior art reference to simply disclose the various elements - the disclosure must show those elements arranged in a manner identical to the arrangement set forth in the claims. The Appellants submit that the disclosure of Casey et al fails to meet this standard.

As applied to the anticipation rejection based on Casey et al, the Applicants would specifically note that, as indicated above, it Casey et al does not even appear to disclose processing conditions specifically applied to **aged undrawn** PTT fibers as required by the present claims. At best, the disclosure of Casey et al is certainly ambiguous on this aspect.

As discussed in detail previously, Casey et al describes cooling the spun fibers at some point (e.g., during the quenching proc-

ess) prior to collection on takeup reels (under tension), then preferably maintaining the collected fibers in a cooled, climate controlled room (see, e.g., the disclosure in Casey et al at lines 11-18 on page 3, and line 26 on page 10 though line 10 on page 11). Prior to removing the fibers from the cooled conditions, Casey et al recommends to make sure the undrawn yarn is under uniform roll tension, with preconditioning prior to drawing occurring under tension as well.

Aged undrawn yarn in the context of the present invention is not on a takeup reel under tension as described in Casey et al. In fact, all the above-mentioned steps taken by Casey et al are specifically to avoid the creation of aged undrawn yarn as that term is understood in the context of the present invention. As indicated previously, while useful, all of the additional conditions used in Casey et al for controlling the aging problem are not practical at commercial spinning speeds and under other commercial conditions.

The Examiner does not address this gap in the disclosure of Casey et al, but instead focuses on the drawing process disclosed in the reference. Even in this limited view, the Appellants submit that the disclosure of Casey et al does not meet the conditions required to anticipate the subject matter of claims 16-30.

In addition to the prewetting step, the claimed process requires that both the first and second drawing stages be conducted under wet conditions as discussed in the present specification in, for example, the paragraph bridging pages 10-11 (and Figure 1), in lines 19-28 on page 12; lines 5-9 on page 13; and lines 10-20 on page 14.

Among other differences, Casey et al does not unambiguously disclose that both drawing steps (when more than one drawing step is used) are conducted under "wet conditions" within the meaning of the presently claimed invention. While Casey et al does seem to disclose a prewetting step (last paragraph on page 11), with respect to the draw steps Casey et al only discloses that "the **initial draw point** of the UDY tow should occur under water..." (emphasis added). The seems to correspond to a "wet" first stage within the context of the present invention, but a discussion of the wetting for the second stage as required by the present claims is totally absent.

The Examiner's view is that Casey et al does in fact disclose a second stage drawing under wet conditions, referring to page 12, lines 12-23, of Casey et al. The Appellants respectfully submit that the Examiner has taken this disclosure of Casey et al out of context.

Specifically, the Appellants would point to the following statement of Casey et al from the passage cited by the Examiner (at lines 16-19):

> "If desired, the second draw stage is hotter than the first draw stage up to a practical maximum of the melting point of the yarn, preferably 60 to 160°C…."

It is not understood how, at the melting point of the yarn (or at 160°C), the second stage draw could unambiguously occur under wet conditions as, for example, a water bath would boil at those temperatures.

Casey et al, therefore, does not disclose (and certainly does not unambiguously disclose) that both drawing steps (when more than one drawing step is used) are conducted under "wet conditions" within the meaning of the presently claimed invention.

Taking all of this into consideration, it is evident that the Casey et al does not disclose the invention as set forth in claim 16 (and other claims dependent thereon), and does not anticipate the claims of the present application for the purposes of 35 U.S.C. §102(b). The Appellants, therefore, respectfully request reversal of this rejection.

With respect to dependent claims 17-30, the Appellants would note that, while these claims are explicitly rejected under 35 U.S.C. §102(b), the Examiner has provided no facts in support thereof. The Examiner has not even provided a basis as to where the limitations of these claims may be found in the disclosure of Casey et al. As such, the Appellants submit that the Examiner has not established a *prima facie* case of anticipation of these claims, and request that the rejection thereof under 35 U.S.C. §102(b) on the current record be reversed as well.

B. FIRST OBVIOUSNESS REJECTION

The Appellants traverse this rejection of claims 16-30 as allegedly being obvious solely on the disclosure of Casey et al.

Admittedly, Casey et al does disclose individually many of the steps of claims 16-30, but also discloses many variations of the same steps that would clearly be outside the present claim scope. As discussed above, Casey et al also appears to fail to disclose applying any of these steps to aged undrawn PTT yarn within the meaning of the present claims.

In any event, in view of the Supreme Court's recent statements in the KSR case (KSR International Co. v. Teleflex Inc., 550 U.S. ___, 2007 WL 1237837, No. 04-1350 slip op. (2007)), the Appellants submit that the determinative question in deciding the appropriateness of this rejection is whether or not the Appellants claimed combination of steps yields predictable results with respect to being able to draw aged undrawn PTT yarn **as required by the present claims.** See also Leapfrog Enterprises Inc. v. Fisher Price, Inc. and Mattel, Inc., No. 06-1402 slip op. at 7 (Fed. Cir. 2007).

As discussed previously, Casey et al provides extensive direction on how to avoid aged undrawn PTT yarn (within the meaning of the present invention), but does not seem to provide coherent direction on how to deal with this problem should it occur. Dealing with this problem is precisely what the present invention is all about.

The Appellants respectfully contend that there is nothing in Casey et al or the current record to remotely suggest that the selection of steps, as embodied in the present claims, would **predictably** result a process that could be used to draw aged undrawn PTT yarn, as required by the present claims. There is simply nothing of record to support selecting steps and operating conditions that may be explicitly disclosed in Casey et al, or modify those steps or operating conditions not explicitly disclosed in Casey et al, in the manner required to achieve the presently claimed invention.

"[A] patent composed of several elements is not proved obvious merely by demonstrating that each of it elements was, independently, known in the prior art." KSR, No. 04-1350 slip op. at 14. Further, the mere fact that the prior art could be modified does not make the modification obvious unless the prior art suggests the desirability of such. See In re Gordon, 221 U.S.P.Q. 1125, 1127 (Fed. Cir. 1984).

Even reaching beyond the specific problem addressed by the Appellants, there is no other evidence of record that any need or problem known in the field of endeavor and addressed by this application would provide a reason for combining the various elements in the manner claimed. Without such evidence, the obviousness rejection cannot stand. See KSR, No. 04-1350 slip op. at 16.

In fact, the only possible way to arrive at the presently claimed invention from the fair disclosure of Casey et al, or the present record as a whole, is with hindsight benefit of the Appellants' disclosure and claims. Hindsight, however, is an inappropriate perspective in which to judge patentability. In re Deminski, 230 U.S.P.Q. 313, 316 (Fed. Cir. 1986).

In view of the above, the Appellants submit that, on the present record, (i) the Examiner has not established a *prima facie* case of obviousness of claims 16-30 based on the disclosure of Casey et al standing alone, and (ii) these claims are in fact patentable over any supportable reading of Casey et al.

The Appellants, therefore, respectfully request reversal of this obviousness rejection as applied to claims 16-30 (and the present claims as a whole).

C. SECOND OBVIOUSNESS REJECTION

The Appellants also traverse the second obviousness rejection of claims 1-15 as allegedly being obvious over the disclosure of Casey et al in view of Hernandez et al.

As set forth by the Examiner in the Final Office Action, Hernandez et al is cited solely for the proposition that PTT fibers having a dpf of 6-25 are known in the literature. The Appellants submit this fact has absolutely no bearing on the present question of obvi-

ousness in view of the established differences between the disclosure of Casey et al and the presently claimed invention.

Hernandez et al does not, in fact, deal with the issue of drawing aged undrawn PTT yarn, and does not otherwise explicitly or implicitly provide guidance to a person of ordinary skill in the relevant art how to modify the disclosure of Casey et al in order to achieve the presently claimed solution. In fact, the Appellants submit that no supportable combination of Casey et al with Hernandez et al even adds up to the presently claimed invention.

As with the first obviousness rejection, the only possible way to arrive at the presently claimed invention from the fair disclosures of the cited art is with the impermissible hindsight benefit of the Appellants' disclosure and claims.

The Appellants, therefore, submit that, on the present record, the Examiner has not established a *prima facie* case of obviousness of claims 1-15, and that these claims are in fact patentable over any supportable combination of Casey et al with Hernandez et al.

As a result, the Appellants respectfully request reversal of this obviousness rejection as applied to claims 1-15 (and the present claims as a whole).

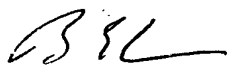
IX. CONCLUSION

As is clear from the above as well as the arguments already of record, the approach taken by the Examiner and the rejections which flow therefrom clearly have no basis in law or fact. The Appellants, therefore, submit that the presently claimed invention is patentable over the art of record, request that the rejections of record be reversed, and further request that the Examiner be directed to:

(i) allow claims 1-30, and

(ii) advance the present application to issue at the earliest possible date.

Respectfully submitted,



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APPENDIX A - CLAIMS APPENDIX

Claims 1-43 from Application Serial No. 10/733,998

1.(Previously Presented) A process for producing 6 to 25 dpf carpet staple fiber comprising the steps of: melt spinning poly(trimethylene terephthalate) into fibers; accumulating the fibers under conditions to produce an aged undrawn yarn; prewetting the aged undrawn yarn, said aged undrawn yarn consisting essentially of poly(trimethylene terephthalate), at a temperature less than about 45°C; drawing the yarn under wet conditions at a temperature of from about 45°C to about 95°C in a first stage to a length of about 30 to about 90 percent of its final length; further drawing the yarn in a second stage at a temperature from about 45°C to about 98°C under wet conditions; crimping the drawn yarn; thermo-fixing the crimped yarn in the presence of steam at a temperature from about 80°C to about 100°C; and drying the crimped yarn at 60°C to 140°C.

2.(Original) The process of claim 1, wherein said undrawn yarn is spun on equipment having a spinneret capillary density of at least 2/cm^2 and a quench zone shorter than about 16 feet.

3.(Original) The process of claim 1, wherein the undrawn yarn is spun at a speed less than about 600 ypm.

4.(Original) The process of claim 1, wherein said prewetting and drawing are carried out under water or under an aqueous solution of processing finish.

5.(Original) The process of claim 1, wherein during said prewetting and drawing, said yarn is in the form of a spun rope of less than about 300,000 denier/inch.

6.(Previously Presented) The process of claim 1, wherein in said first draw stage, the yarn is drawn to a length from about 40 to about 70 percent of its final length.

7.(Previously Presented) The process of claim 1, wherein in said first draw stage, the yarn is drawn to a length from about 50 to about 55 percent of its final length.

8.(Original) The process of claim 1, wherein said first draw stage is carried out at a temperature of about 80°C or less.

9.(Original) The process of claim 1, wherein said first draw stage is carried out at a temperature of about 70°C or less.

10.(Original) The process of claim 1, wherein said first draw stage is carried out at a temperature of about 60°C or less.

11.(Original) The process of claim 1, wherein said first draw stage is carried out at a temperature of about 50°C to about 55°C.

12.(Original) The process of claim 1, wherein said second draw stage is carried out at a temperature of about 60°C to about 80°C.

13.(Original) The process of claim 1 wherein said thermo-fixing is carried out at a temperature of about 85°C.

14.(Original) The process of claim 1 wherein said drawn yarn has a denier of 6 to 20 dpf.

15.(Previously Presented) The process of claim 1 wherein the crimped yarn is dried at a temperature from about 60°C to about 100°C.

16.(Previously Presented) A process for producing 1 to 6 dpf textile staple fiber comprising the steps of: melt spinning poly(trimethylene terephthalate) into fibers; accumulating the fibers under conditions to produce an aged undrawn yarn; prewetting the aged undrawn yarn, said aged undrawn yarn consisting essentially of poly(trimethylene terephthalate), at a temperature less than about 45°C; drawing the yarn under wet conditions at a temperature of from about 45°C to about 95°C in a first stage to a length of about 30 to about 90 percent of its final length; further drawing

the yarn in a second stage at a temperature from about 45°C to about 98°C under wet conditions; crimping the drawn yarn; thermo-fixing the crimped yarn in the presence of steam at a temperature from about 80°C to about 100°C; and drying the crimped yarn at 60°C to 140°C.

17.(Original) The process of claim 16, wherein said undrawn yarn is spun on equipment having a spinneret capillary density of at least about 8/cm^2 and a quench zone shorter than about 16 feet.

18.(Original) The process of claim 16 wherein said undrawn yarn is spun at a speed of 1300 ypm or less.

19.(Original) The process of claim 16 wherein said undrawn yarn is spun at a speed of 900 ypm or less.

20.(Original) The process of claim 16 wherein said prewetting and drawing are carried out under water or under an aqueous solution of processing finish.

21.(Original) The process of claim 16, wherein during said prewetting and drawing, said yarn is in the form of a spun rope of less than about 200,000 denier/inch.

22.(Previously Presented) The process of claim 16, wherein in said first draw stage, the yarn is drawn to a length from about 40 to about 90 percent of its final length.

23.(Previously Presented) The process of claim 16, wherein in said first draw stage, the yarn is drawn to a length from about 70 to about 90 percent of its final length.

24.(Original) The process of claim 16, wherein said first draw stage is carried out at a temperature of about 80°C or less.

25.(Original) The process of claim 16, wherein said first draw stage is carried out at a temperature of about 70°C or less.

26.(Original) The process of claim 16, wherein said first draw stage is carried out at a temperature of about 60°C or less.

27.(Original) The process of claim 16, wherein said first draw stage is carried out at a temperature of about 50°C to about 55°C.

28.(Original) The process of claim 16, wherein said second draw stage is carried out at a temperature of about 60°C to about 80°C.

29.(Original) The process of claim 16, wherein said thermo-fixing is carried out at a temperature of about 85°C.

30.(Previously Presented) The process of claim 16, wherein said crimped yarn is dried at a temperature from about 60°C to about 100°C.

31.(Canceled)

32.(Canceled)

33.(Canceled)

34.(Canceled)

35.(Canceled)

36.(Canceled)

37.(Canceled)

38.(Canceled)

39.(Canceled)

40.(Canceled)

41.(Canceled)

42.(Canceled)

43.(Canceled)

44.(Canceled)

45.(Canceled)

APPENDIX B - EVIDENCE APPENDIX

Application Serial No. 10/733,998

1. WO01/68962 (entered into the record in the First Office Action dated 8 June 2006)

2. US2002/0071951A1 (entered into the record in the First Office Action dated 8 June 2006)

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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(54) Title: POLY(TRIMETHYLENE) TEREPHTHALATE TEXTILE STAPLE PRODUCTION

(57) Abstract: A process for making textile staple fibre from polytrimethylene terephthalate (PTT) which comprises: (a) melt extruding PTT polymer at 245 to 253 °C, (b) spinning the extruded PTT into yarn using at least one spinneret, (c) moving the spun yarn to a first takeup roll wherein the distance from the spinneret to the roll is from 16 to 20 feet, (d) cooling the spun yarn to less than 31 °C before it reaches the roll, (e) prior to the draw process, preconditioning the yarn under tension at a temperature of at least 60 °C, (f) drawing the yarn at a temperature of at least 60 °C, (g) allowing the drawn yarn to relax at a temperature of up to 190 °C, and (h) crimping the drawn yarn at a temperature of 70 to 120 °C, and decreasing the drawn yarn feed denier into the crimper by 10 to 60 percent by denier.

POLY(TRIMETHYLENE) TEREPHTHALATE TEXTILE STAPLE PRODUCTION

Field of the Invention

Poly(trimethylene terephthalate) polymer is a new polyester resin suitable for use in carpet, textile, and other thermoplastic resin applications. Poly(trimethylene terephthalate) (PTT) is chemically an aromatic polyester resin made by the polycondensation of 1,3-propanediol (PDO) and terephthalic acid. Production of textile staple from PTT is possible on a wide variety of commercial processing equipment.

Background of the Invention

PET synthetic fiber staple production is often decoupled two-stage process. The first stage involves extrusion of Un-Drawn Yarn, which is stored for draw processing in the second stage. There are two main types of draw processes used in staple production Draw-Relax and Draw Anneal. The fundamental difference between these two processes is how fiber shrinkage is managed. In draw relax staple production the shrinkage strategy is to pre-shrink the fibers in an oven after crimping to desired performance and properties. In draw annealed staple production the shrinkage strategy is heat the fibers allowing for constant length crystallization before crimping.

Staple fibre from polyethylene terephthalate (PET) has been produced and there are well established processes for doing so. It would be desirable to be able to produce PTT staple fibre on existing equipment. However, there are many differences between the two polymers which make the production of commercially useful staple fiber of PTT on existing staple production equipment difficult or unlikely. To understand how

to produce PTT staple on existing equipment one needs to address several process questions:

How do you characterize the draw behavior of undrawn yarn? How does the draw behavior of undrawn yarn change over time? As described in Example #1.

How do you control the properties of undrawn Yarn during extrusion? As described in Example #2.

What is the typical draw performance for the undrawn yarn. As described in Example #3 and Example #4.

How does one control fiber shrinkage during undrawn Yarn production and storage as described in Example #5.

How do you control fiber shrinkage during the staple draw and in the final staple products? As described in Example #6.

How does one crimp the fiber to provide texture and cohesion in downstream commercial processes for staple textile spun yarns and non-wovens? As described in Example #7

How do you heat set and control the youngs modulus and stretch properties of the staple fiber. How do the staple fiber properties impact the properties of spun yarns? As described in Example #8.

What is a basic process to produce staple on existing equipment that addresses the interdependent nature of the first six process questions discussed above. Such a process is provided by the present invention.

Summary of the Invention

The present invention describes a two-stage staple production process using PTT. The first stage is extrusion of

undrawn yarn (UDY). UDY is converted to a staple fibre product in the second draw production stage.

In accordance with the present invention there is provided a process for making textile staple fibre from polytrimethylene terephthalate (PTT) on existing PET textile staple fibre making equipment which comprises: (a) melt extruding PTT polymer at 245 to 253° C, preferably 245 to 250 °C, (b) spinning the extruded PTT into yarn using at least one spinneret, (c) moving the spun yarn to a first takeup roll wherein the distance from the spinneret to the first takeup roll is from 16 to 20 feet, (d) cooling the spun yarn to less than 31°C, preferably less than 25 C, more preferably less than 20 C, before it reaches the first takeup roll, (e) optionally, storing the spun yarn in a climate controlled room at a temperature of no more than 31°C (both this step and the previous one are carried out to minimize premature shrinkage of the undrawn yarn prior to draw processing), (f) prior to the draw process, preconditioning the yarn under tension at a temperature of at least 60°C, preferably 60 to 100°C, (g) drawing the yarn at a temperature of at least 60°C, preferably 60 to 100°C, with an optional preferred second draw wherein the majority of the total draw occurs in the first draw, most preferably 80 to 85% of the total draw, and wherein the second and subsequent draws are carried out at a temperature above the temperature of the first draw up to a practical maximum of the melting point of the yarn, preferably 60 to 160°C, most preferably at a temperature of 80 to 100°C, (h) allowing the drawn yarn to relax at a temperature of up to 190°C , preferably 100 to 140°C (the relaxation can be from 2 to 25% or possibly more but is preferably 2 to 10%) in order to achieve an increase in the initial Young's modulus of the drawn yarn, and (i) crimping the drawn yarn at a temperature of 70 to 120°C, preferably 80 to 120°C if the relaxation step is used and 70 to 100°C if it is not used, and decreasing the drawn yarn feed denier into the crimper by 10 to 60 percent by denier, preferably 40 to 60

percent, from the drawn yarn feed rate used for making comparable PET staple in the existing equipment. Also, alternatively or in combination, the volume of the crimper may be increased 10 to 50, preferably 20 to 35 percent more than the crimper volume used to make PET in the existing equipment. Preferably, the choice of conditions is based on the particular equipment and the desired yield.

Brief Description of the Drawings

The present invention will now be described by way of example with reference to the accompanying drawings, in which:

Figure 1 is a schematic of the process steps from resin to baled fibre whose critical elements will be described.

Figure 2 is the tenacity elongation balance curve useful in helping assess the possible range of staple properties for PTT.

Figure 3 shows a typical Stress / Strain Curve for as Spun Yarn Bundles.

Figure 4 shows the effect of extrusion temperature on fiber drawability.

Figure 5 shows the undrawn yarn shrinkage in water of different temperatures as a function of undrawn yarn spinning conditions.

Figure 6 shows the orientation schematic describing the effect of fiber shrinkage.

Figure 7 shows the effect of draw bath temperature and total orientation parameter on boil off shrinkage;

Figure 8 shows the effect of draw bath temperature and total orientation parameter on 125°C dry heat shrinkage.

Figure 9 shows the effect of draw bath temperature and total orientation parameter on 140°C dry heat shrinkage.

Figure 10 shows the effect of draw bath temperature and total orientation parameter on 175°C dry heat shrinkage.

Figure 11 shows the effect of draw bath temperature and total orientation parameter on 197°C dry heat shrinkage.

Figure 12 shows the effect of draw ratio and draw bath temperature on draw process relaxation factor.

Figure 13 shows the predicted dry heat shrinkage as a function of drier (relaxer) oven temperature for free relax 1.4 Total Orientation Parameter and 75°C draw bath temperature.

Figure 14 shows the effect of relaxer oven temperature and applied yarn stretch on 175°C dry heat shrinkage for 100% PTT yarns.

Figure 15 shows the effect of relaxer oven temperature and applied yarn stretch on 175°C dry heat shrinkage for 100% PET yarns.

Figure 16 shows the comparison of PTT and PET spun yarn 175°C dry heat shrinkage at two yarn heat set temperatures.

Figure 17 shows the effect of relaxer oven temperature and applied yarn stretch on 175°C dry heat shrinkage for 50:50 PTT:Cotton yarns.

Figure 18 shows the comparison of PTT and PET spun yarn boil off shrinkage at two heat set temperatures.

Figure 19 shows the comparison of PTT and PET spun yarn load at 5% strain at two yarn heat set temperatures.

Figure 20 shows the comparison of PTT and PET spun yarn 2 minute percent stress decay at two spun yarn heat set temperatures.

Figure 21 shows the comparison of PTT and PET spun yarn percent strain recovery (2 minute extension) at two spun yarn heat set temperatures.

Detailed Description of the Invention

Polymer textile staple is feasible using existing facilities. Since the equipment used by different companies varies greatly, there will be differences in how the processes are carried out. Once the staple producer tailors its settings to the unique properties of PTT, it is possible to produce a wide variety of staple products suitable for use in spun yarn and non-woven textiles. Textile staple produced from PTT offers excellent loft and drape providing softness, bulk, compatibility in blends, easy-care, and shape retention in textile products.

1.0 POLYMER MELTING

1.1 Resin Transfer and Drying

Low energy air conveying systems minimize dust formation when transferring resin from shipping containers, processing equipment and storage facilities. Before extrusion, PTT resin should be dried to a constant moisture level of 50 ppm or less. This moisture specification minimizes the impact of resin degradation by hydrolysis during melt spinning. Many types of commercial dryers using desiccated air have successfully met

this requirement. Dryers equipped with molecular sieves (13X & 4A), vacuum systems, and lithium chloride desiccants have met moisture requirements in commercial production. When possible, it is preferable to dry the polymer using 13X molecular sieve desiccated air (dew point of -40°C or less) heated to 130°C with 4-6 hours of drying time. Using dry air when transferring dried resin from the dryer to the extruder is essential to minimize hydrolysis during melt spinning.

In large commercial dryers, drying PTT at rates that can keep pace with extrusion throughput may be challenging. In this situation higher dryer temperatures may be needed. The PTT dryer air temperature should not exceed 165°C. Dryer residence time should not exceed 4 hours when using 165°C air.

1.2 Undrawn Yarn (UDY) Extrusion

A typical melt preparation system includes an extruder, spin beam, melt pump, and spin pack. The key is to establish a uniform, optimum polymer melt viscosity by minimizing melt process temperature and residence time. Commercial production of PTT UDY with both twin screw and single screw extruders is straightforward. In twin screw extruders it may be necessary to reduce the extruder melt pressure by as much as 25-50% (from PET conditions) to avoid excessive shear degradation of the polymer melt. Commercial production of PTT UDY uses extruder melt temperatures ranging from 245°C to 270°C. Care must be taken when producing PTT UDY at melt temperatures between 260 to 270°C to avoid excessive degradation of polymer melt and subsequent UDY properties. The optimal staple extrusion melt temperature for PTT is 245 to 253°C, preferably 245 to 250°C. Future PTT resins with lower intrinsic viscosity will likely require lower temperatures. Figure 4 shows that better drawability is obtained when the polymer is extruded at 250°C rather than at 240°C or 260°C.

2.0 UNDRAWN YARN (UDY) SPINNING

2.1 Spin Beams, Pumps, and Packs

Trials using mono-component and bi-component extrusion systems to produce PTT staple UDY were successful. Spin pump volume and revolution control systems sized for PET usually meet the lower through put per position requirement for PTT staple. The filtration media should have minimum pore size of 30 microns. Often commercial spin packs use a minimum amount of filtration media. In the early stages of developing a PTT staple production process, it is preferable to use a standard filtration depth of medium/course sand (90/120 mesh). Evaluation of filament diameter uniformity will help determine if spin pack filtration or extrusion system melt pressure need optimization.

Staple extrusion systems are engineered for a specific range of resin viscosity, throughput, melt temperature, and residence time. In general, the hole-throughput needed to make PTT staple is usually 20-30% lower than that for PET products of comparable denier. This essentially increases the residence time for PTT extruded with PET staple production equipment. The increase in melt residence time can lead to degradation if melt temperatures are higher than 260°C. Transfer line and spin beam heating systems should equal the extruder outlet polymer temperature if possible.

2.2 Spinnerets

Spinneret selection depends on the target product denier and is determined by the limiting throughput per hole-minute for stable melt spinning. In general PTT staple can use standard PET spinneret designs for similar products. However, PTT staple generally requires smaller capillary diametres for low denier products when compared to PET staple production. PTT resins have an upper shear rate limit of 7500-9000

reciprocal seconds for round cross sections depending on melt extrusion conditions.

Spinneret selection based on target staple product denier is shown in Table I.

Table I: Spinneret Selection Chart

Fine Denier Range at 1100m/ min	1.0-1.3 dpf	1.30-1.75 dpf	1.40-1.85 dpf
Spinneret diameter (mm)	0.23	0.25	0.35
Spinneret l/d	1.85	1.85	1.85-2.0
Limiting Throughput per hole	0.32	0.41	0.45

It is important that a long fibre culmination zone (the distance from the spinneret to the take up roll) be used. This means that the zone should be 16 to 20 feet rather than the standard 8 to 12 feet for PET. In process shrinkage of PTT UDY is relatively high so the process must allow the fibre to establish a stable molecular structure before all of the filaments are combined into one large draw process feed yarn. In the production of PET staple fibre, this is not a significant problem. PTT has a more elastic crystalline morphology so the longer fibre culmination link helps stabilize the yarn allowing a manufacture to avoid additional air conditioning costs.

2.3 Quench

Trials using cross flow and radial quenching systems were successful. Radial quenching systems with both inside-to-outside and outside-to-inside airflow have been used successfully. The fibre bundle should be quenched quickly and uniformly to prevent UDY shrinkage in the spun supply cans. Quench temperatures ranging from 8-35°C have been used, although temperatures of 8-25°C are preferred. In general, quench airflow rates are limited by operability of the UDY thread path. The number of filaments per position has ranged from 350 to 3500 filaments per position. In fine denier staple

production it may be possible to have upwards of 6250 filaments per position with modern radial quenching systems. Optimization of quench systems involves determining which conditions offer the most operability and yield the highest percent elongation for the target UDY creel properties.

2.4 Spin Finish

In this specification all the coatings applied to the PTT fibre during staple extrusion and draw production are defined as spin finishes. Spin finishes are fibre coatings that provide lubrication, cohesion, and additive protection to the PTT fibre during staple production and down stream processing. Both multi-component phosphate and mineral oil based finishes have been used successfully in the production of PTT staple. Proven PET spin finish chemistries and application methods are satisfactory for initial PTT staple products. Spin finish formulations and application methods can then be changed based on customer feedback on staple processing.

2.5 Take-Up

Take up speeds ranging from 900 to 1250 metres per minute have been used for commercial PTT UDY production. On research equipment, take up speeds for UDY have ranged from 500 to 2250 metres per minute. It is useful to take a controlled relaxation between the take-up capstan rolls and sunflower wheel before piddling into the tow can. Cooling all the filaments in a single position to less than 25-30°C is necessary to minimize UDY shrinkage in the tow can.

3.0 TOW DRAWING AND FINISHING

3.1 UDY Storage

Under normal storage conditions, PTT UDY completes over 90% of its ageing process within 8 hours of extrusion. UDY draw properties stabilize within 24 hours and no significant change in draw properties is observed after 2-4 months of storage at

constant temperature. PTT UDY has the potential to shrink more easily and at lower temperatures than PET UDY. Storage conditions warmer than 25-30°C should be avoided because they trigger UDY shrinkage. Ideally, the PTT UDY creel is stored in an air-conditioned environment to help avoid shrinkage. The exact temperature that triggers PTT UDY shrinkage depends on UDY extrusion, quench, take-up and storage conditions. Even if the PTT UDY shrinks it is possible to convert this UDY into a first grade commercial staple product during draw processing with minor impact on product quality.

3.2 Creel Size

The creel size for PTT staple is determined by the size of the production crimper. In general the creel size for PTT staple is roughly 60% of an equivalent PET staple product because of the higher bulk of PTT fibres. A 600,000 denier drawn tow will satisfactorily feed a 110 mm wide by 20 mm high crimper. This may change as crimper size increases and/or draw production rates increase above 100-130 metres per minute. Since most draw production lines have a maximum line speed of 250-300 m/min, increasing the volume of the crimping chamber is another way to improve draw line productivity.

3.3 Creel and Tow Preparation

Avoid heating the PTT UDY above 25°C until the UDY tow is under uniform roll tension. This will minimize the shrinkage of PTT feeding the draw process and maintain a uniform fibre tension at all points in the tow cross section during drawing. If uncontrolled, non-uniform UDY shrinkage is allowed, can to can orientation variation will limit draw process uniformity.

Prewet baths before drawing are preferred, but the temperature should not exceed 25°C unless driven and nipped rolls are provided to minimize tension into the draw feed section. If driven rolls are not available, the bath should be at the lowest uniform temperature possible.

3.4 Drawing Process

PTT staple has been manufactured on draw-relax and draw-anneal process configurations. In the draw relax process the staple is heat treated and dried under zero tension to reduce shrinkage. This process produces a low modulus fibre suitable for PTT spun yarns and blending with low modulus fibres like wool and acrylic. The draw anneal process heat treats the tow on rolls under high tension and produces a higher modulus fibre more suitable for blending with minor amounts of rayon, cotton or other higher modulus fibre.

The initial draw point of the UDY tow in the first draw stage should occur under water heated to a minimum of 60°C, preferably 60 to 100°C. Keeping the draw point hot improves draw process performance by significantly reducing the impact of extrusion conditions on production draw ratios. If desired, the second draw stage is hotter than the first draw stage up to a practical maximum of the melting point of the yarn, preferably 60 to 160°C, most preferably 80-100°C. Unlike PET, PTT will not turn harsh in heated draw baths. Additional draw zones are optional and usually extend the total machine draw ratio slightly. The major draw ratio should be taken in the first stage.

Annealing or relaxing PTT staple tow with a 3% roll relaxation across a set of 100-130°C calendar rolls increases the initial modulus of the final PTT staple by 12-14%. This process produces a high modulus fibre suitable for PTT spun yarns and blending with high modulus fibres like cotton, rayon, and PET. Initial modulus increases about 4% for every 10°C from 130-150°C when the relaxation across the roll set is held at 3%. Annealing PTT tow above 150°C may require increasing the relaxation across the calendar rolls to avoid excessive filament breakage. Spin finish is often applied to make up for spin finish lost in draw processing using a dip bath or

front/back kiss roll application just before the crimping stage.

3.5 Crimping

PTT tow bends very easily compared to PET tow given its low bending modulus. This low modulus also gives PTT excellent hand and softness. Additionally, PTT is much more bulky than PET. Low bending modulus and high bulk require the following changes in crimping conditions:

- Dancer roll and crimper roll are reduced to provide more control of crimp geometry.

- Feed tow denier must be decreased or crimper volume increased because of PTT's higher bulk. The increased bulkiness of PTT can be accounted for by either decreasing the amount of tow denier feeding to the crimper by most preferably 10 to 60 percent, preferably 40 to 60 percent, all by denier. Another way is to increase the volume of the crimper by 10 to 50 percent, preferably 20 to 35 percent, all by volume. Also, a combination of these two methods can be used.

- Ideally, the crimper should be equipped with steam and spin finish injection to better control crimping chamber temperature.

- It may be necessary to improve the precision of pressure and temperature control in the crimping chamber.

Crimp stability and take up improve significantly when the crimper chamber is at least 85°C and at 300 kPa (3 bar) of gate pressure. Crimp frequency may be higher and crimp amplitude lower than comparable PET staple. Crimp stability and take up improves as crimper temperature increases. The crimper should not be heated too much because, as crimp stability increases, so does staple cohesion, which can increase defects in carding.

3.6 Drying, Cutting, and Packaging

Relaxation (drying) of PTT staple in conventional belt ovens is straightforward. However, both crimp geometry and shrinkage characteristics change as the oven temperature is raised above the hottest temperature in the preceding draw process. In draw relax staple production both staple fibre and subsequent spun yarn dry heat shrinkage decrease as the dryer temperature is increased.

In draw anneal staple production the relaxation oven is used as a dryer. The airflow rates are relatively high and the air temperature relatively low (75-90°C) to facilitate tow drying. These conditions are not hot enough to allow staple fibre relaxation or crimp geometry change. Staple tow has been cut in commercial production using both rotary and pacific converter type cutters without modification. Both gravity and air conveyed staple balers have packaged PTT staple in commercial trials.

4.0 GENERIC RECIPES FOR 1.7, 2.5 AND 3.33 DTEX (1.5, 2.25, AND 3 DPF) STAPLE

Draft recipes for three typical staple products are briefly outlined in the following table. Every staple production facility is different. It will usually take 2-3 attempts on a commercial line to identify acommercial process for PTT staple. These recipes were developed on small commercial production equipment. They may change slightly as processes are scaled up to larger equipment and higher production rates. The UDY is produced using a 253°C melt temperature at 1100 m/min. To attain these draw ratios requires uniform extrusion conditions such that the filament diameter coefficient of variation is between 3-5% in all spinning positions. Further these draw ratios are obtained in very well controlled, modern process equipment. It is not unusual for older equipment to only attain 75-85% of these draw ratios.

The recipes in table II also describe a high and low shrinkage recipe for each target staple denier. The amount of draw production shrinkage decreases significantly as the first stage draw bath temperature is raised above 60°C. Further the amount of draw production shrinkage decreases slightly as the draw ratio increases. Lastly draw production shrinkage in the crimper and dryer are further reduced when using calendar rolls to anneal the fibre. Commercial product draw production rates of 100-130 metres per minute and development draw rates as high as 225 m/min have been used. The commercial draw relax process typically uses a 70°C first draw and a 100°C second draw. The commercial annealed staple process typically uses a 70°C first draw, a 100°C second draw, and 130°C calendar rolls with a 0.95 relaxation.

Table II: Draft Recipes for 1.5, 2.25, 3.0 dpf Staple

Undrawn Yarn dpf	4.0 dTex	3.2 dTex	6.4 dTex	6.8 dTex	9.2 dTex	9.7 dTex
1st Draw Ratio $D^2/_1$	2.73	2.73	2.74	2.74	2.75	2.75
2nd Draw Ratio $D^3/_2$	1.10	1.10	1.15	1.15	1.20	1.20
Machine Draw Ratio	3.00	3.00	3.15	3.15	3.30	3.30
Draw Production Relaxation in Crimper & Dryer	High	Low	High	Low	High	Low
	20%	16%	18%	14%	16%	12%
Final Staple Product	1.7 dTex	1.7 dTex	2.5 dTex	2.5 dTex	3.3 dTex	3.0 dTex

4.1 STAPLE PROPERTIES

This discussion of tensile properties assumes that the creel stock is drawn to within 90% of tow breakout. A typical draw relax PTT staple fibre will usually have a tenacity of 2.7-3.0 cN/dTex and an elongation between 80-90%. A typical commercial draw annealed staple will have 3.4-3.5 cN/dTex and an elongation between 60-65%. The tenacity elongation balance curve below (Figure 2) is useful in helping assess the possible range of staple properties for PTT. High tenacity, low elongation PTT staple is very challenging to produce due to rapid relaxation of PTT tow under crimping conditions. Single filament test results on R&D equipment indicate fibre tenacities as high as 4 cN/Tex with 45% elongation. One may be able to produce PTT staple with tenacities greater than 3.5 cN/Tex on a highly optimized draw anneal process. In this effort the control of crimping conditions will be critical.

Example 1: Controlling Shrinkage of Undrawn Yarn During Extrusion and Storage

Evaluation of the undrawn yarn shrinkage of PTT UDY spun at two different locations under a wide variety of different conditions. Test results indicate that it is best to store PTT UDY below 31°C to avoid excessive shrinkage greater than 2-3%, as shown in Figure 5. This chart shows the percentage shrinkage in undrawn yarn immersed in water baths at several temperatures - 30°C, 31°C, 32°C and 35°C. The spinning conditions covered a range of drawn product denier per filament (dpf) range from 0.8 to 4.5 dpf and the operating range of throughput and takeup speed for different developmental staple production lines one at location A and another at Location B. This chart also shows that PTT UDY shrinkage is more a function of spinning conditions than quench air temperature. Location A uses 25°C quench air and location B uses 16°C quench air.

Excessive undrawn yarn shrinkage is undesirable because it can increase staple product variability if not properly controlled.

Example 2: Shrinkage of Staple Process Drawn PTT Ribbons

Summary and Conclusions:

Drawing in baths of 60°C or higher eliminates any effect of spin induced structure on as drawn fibre shrinkage.

Drawn fibre shrinkage decreases with increasing draw bath temperature, but the effect is fairly small at temperatures above 60°C. Shrinkage also decreases with increasing total orientation (Draw Ratio), but the effect is very minimal at the higher draw bath temperatures. When as drawn shrinkage is insensitive to spinning and drawing settings, crimping becomes more stable, and the product less variable. Drawing at temperatures above 60°C is recommended and should provide stable crimping operation.

Predicted relaxation factors for crimping and drying/relaxing as a function of drier/relaxation temperature were prepared from the shrinkage data. Although the shape of the curve is correct and can be used for extrapolation of known data, the magnitude of the factor appears too high.

It appears unlikely that product shrinkage as a function of drier / relaxation temperature can be predicted from shrinkage data for PTT.

Introduction

The range of spinning conditions examined on the pilot draw line used herein were:

- 240 to 260°C block temperature
- 0.432 to 0.865 g/hole min (0.4 mm capillary)
- 1000 to 2000 m/min spin speed

These supplies were drawn at three draw ratios:

- Breakout Draw Ratio (BODR) minus 0.1
- BODR - 0.2
- BODR - 0.4

This, coupled with the large variation in spun orientation, gives a large range of spun orientation.

Three staple draw bath temperatures were used:

- 40°C
- 55°C
- 70°C

This was the maximum practical operable range for the equipment.

Drawn ribbons were completely characterized. The shrinkage results are analyzed below.

Unlike tenacity and elongation, which in PTT, PET, and other melt spun polymers, is primarily a function of total orientation, shrinkage is a much more sophisticated probe of fibre structure, and is affected by orientation and, more importantly, by crystallinity.

The objective of this part of the experiments is to answer the following shrinkage questions, which are presented in their order of importance to process design.

1. Do differences in spin yarn structure persist through drawing, or does the drawing process erase them? This has important implications in the design of spin processes and procedures.

2. How does the draw bath temperature affect shrinkage? Residual shrinkage after drawing is a major factor affecting how easily a fibre can be crimped. In general, fibres with high shrinkage crimp easily. If shrinkage is a strong function of draw bath temperature and orientation, the crimper must frequently be rebalanced to reflect changing draw conditions, and crimping is less uniform.

3. How much shrinkage will occur when a fibre is drawn and crimped and how is it affected by spin and draw conditions? This information is used to calculate the relaxation factor in the spinning model.

4. What additional product shrinkage will exist at higher temperatures when fibre is free relaxed in an oven at a given temperature?

A model that has proven useful for PET has the following premises:

When heated above glass transition temperature, unless restrained, a fiber will shrink until all the amorphous area has deoriented.

As temperature is raised above glass transition, additional oriented amorphous areas appear as crystals melt. These newly created amorphous areas then deorient, providing additional shrinkage. So, in general, the higher the temperature, the higher the shrinkage.

Several definitions, which are somewhat circular in nature, are now required. Glass transition temperature is defined as that temperature at which unrestrained amorphous chains are free to deorient, as required by the second law of thermodynamics. Amorphous areas are those which are not crystalline. Crystalline areas are those which do not deorient at this temperature. There are any number of ways to define crystalline regions in terms of TGA curves, X-ray behavior, density etc, and all give more or less different, but related, answers in terms of % crystalinity. For the purposes of this discussion we will define crystals in terms of their ability to retain orientation at temperature.

Inherent in this model is the assumption that heat treating a rope results only in crystalline melting and fibre deorientation. For PET yarns relaxed in processes with short

dwell times, this model works well. It works fairly well for staple processes involving dwell times of several minutes, but its validity for PTT was unknown before this work.

The length, orientation diagram in Figure 6 can be used to illustrate the process. This diagram represents what happens when you draw a fibre from its length at zero birefringence to the sample fibre length, l_f. When this fibre is heated to temperature T_1 it loses length to l_1 because all the amorphous areas deorientate and all crystals that are not stable to T_1 melt and also deorientate.

The fibre does not deorientate completely, because there are still crystals that are stable at T_1. When the temperature is raised to T_2, additional crystals melt, become amorphous, deorientate, and the length decreases further. One would think that it would be possible to shrink completely to zero birefringence draw ratio 1.0, but in practice there are some crystals that are stable to and beyond the melting point, (which causes problems in PET polymerization). These do not deorient and so reorientation can never be complete.

With the above introduction behind us, it is now possible to address the experimental questions.

Do differences in spin yarn structure persist through drawing?

One would expect that shrinkage should be a strong function of the draw ratio, because that is what provides the orientation that is lost. With PET, this is true to some degree, but the effect is grossly overshadowed by the fact that as orientation increases, so does the ability to form crystalline areas, so there are opposing effects of orientation increase. Also in PET, at elevated draw bath temperatures, all memory of spinning is erased, in so far as shrinkage is concerned. Orientation can be approximated as the total

orientation parameter (TOP) (Denier Draw Ratio / Natural Draw Ratio).

To calculate the natural draw ratio, it is necessary to determine the proper strain rate for the laboratory equipment and skills which would give reproducible results. A single tube spun at 40#/hr, 240°C, and 1500 m/min was tested at strain rates from 200 to 800 % per minute. Three replicate measurements were performed with the curves traced on a single graph. Results were quite reproducible at all strain rates indicating good laboratory skills and equipment. All determinations gave the characteristic curve illustrated in Figure 3. Natural draw ratio can be calculated easily from these plots as follows:

$$NDR = 1 + (S_n / 100) \qquad (1)$$

where:

S_n is % Strain at the Natural Draw Strain

This is equivalent to the classic definition of NDR which is:

$$NDR = l_d / l_s \qquad (2)$$

where:

l_d is the length at the natural draw point of inflection

l_s is the length of the spun sample.

The first step is to establish what variables are statistically significant in predicting shrinkage at a given temperature. The procedure was to use the stepwise forward and stepwise backward regression procedures in Sigma Stat 2.0 with F to enter >4.0 and P to reject <0.05.

Results summarised in Table III indicate:

- Both procedures were in general agreement.
- At draw temperatures of 60°C or higher, spinning variables play no significant role in drawn fibre shrinkage.
- Total Orientation Parameter and, surprisingly, block temperature were weakly significant factors in shrinkage at the 45°C draw temperature.

It is concluded that draw temperatures of 60°C or higher should be used to wipe out any spinning effects on product shrinkage. This data supports the hypothesis that, like PET, spinning structure is wiped out if a draw temperature significantly above T_g is used. Regression equations for correlations with r^2 >0.5 are reported below the Table. Note that there are no such for T>= 60°C.

Table III

Regression Analysis of Ribbon Shrinkage

Draw Bath Temperature, °C	Shrinkage	Forward Test		Backward Test	
		Variables	r^2	Variables	r^2
45	Boil Off	TOP, T_b	0.666	TOP, T_b	0.666[1]
"	125 °C	TOP, T_b	0.695	TOP, T_b	0.695[2]
"	140 °C	TOP, T_b	0.540	TOP, T_b	0.540[3]
"	175 °C	TOP, T_b	0.489	TOP, T_b	0.441
"	197 °C	TOP	0.126	TOP	0.126
60	Boil Off	Q_h	0.190	Q_h	0.153
"	125 °C	TOP	0.188	Q_h	0.131
"	140 °C	TOP	0.241	TOP	0.241
"	175 °C	AVE	na	AVE	na
"	197 °C	AVE	na	AVE	na
75	Boil Off	AVE	na	AVE	na
"	125 °C	Q_h, S_m	0.273	Q_h, S_m	0.273
"	140 °C	AVE	na	AVE	na
"	175 °C	AVE	na	AVE	na
"	197 °C	AVE	na	AVE	na

TOP = Total Orientation Parameter = (Denier Draw Ratio/Natural Draw Ratio)
T_b = Block Temperature, °C
Q_h = Hole Throughput, g/hole minute
S_m = Spinning Speed, metres/minute
AVE = All Independent Variables Eliminated

How does the draw bath temperature affect shrinkage? Figures 7 through 11 are plots of Boil Off Shrinkage, and Dry Heat Shrinkage at 125,140, 175, and 197°C, for the three draw bath temperatures used. It is clear that there is a large mechanism change between 45 and 60°C, the next higher temperature tested. At temperatures greater than 60°C shrinkage is nearly independent of orientation, and relatively insensitive to bath temperature.

Higher bath temperatures do decrease shrinkage potential a small amount, but not significantly in terms of crimping potential or probable product performance.

Operation at temperatures of 60°C or higher is recommended because crimper operation is greatly simplified. Crimper adjustments under these conditions are not required except to compensate for denier density into the crimper (denier/linear crimper inch, dtex/linear crimper cm).

How does spinning and draw bath temperature affect the relaxation factor? Figures 7 through 11, and the analysis of variance, indicate that shrinkage potential of drawn rope is independent of spinning conditions and only weakly dependent on orientation, except for the lowest temperature examined, 45°C.

Figure 12 shows the relationship between oven temperature and relaxation factor for drawn ropes. At draw bath temperatures above 60°C a line through the top grouping of data points should approximate the relaxation factor. This is a good starting point, but the value may be too high (shrinkage too low) because the shrinkage method uses a small weight on the sample so it is not completely free to relax as it would in a typical plant drier/relaxer.

However, the curve should have the correct shape and therefore be good enough to extrapolate the temperature effect when more machine specific data is obtained.

Can relaxed product shrinkage be predicted from the ribbon shrinkage data?

Referring to Figure 3 and the simple shrinkage model for PET it is found that if a fibre at l_f is put in an oven at T_1, it will lose amorphous orientation and some of the crystals will melt and deorientate and its length will decrease to length l_1. Similarly, if a sample of length l_f is placed in an oven at T_2, which is higher than T_1, it will shrink more because more of the crystalline material will melt at the higher temperature and shrink to length l_2.

Mathematically, the shrinkage may be expressed in the following way:

Let: Φ_1 = % Shrinkage @ T_1 / 100 (1)

Φ_2 = % Shrinkage @ T_2 / 100 (2)

Then, from the definition of Dry Heat Shrinkage:

$$\Phi_1 = (l_f - l_1)/l_f = 1 - l_1 / l_f \quad (3)$$

$$\Phi_2 = 1 - l_2 / l_f \quad (4)$$

What would happen if the sample free relaxed at T_1 is tested it for shrinkage at T_2? If no crystalline growth or change other than melting and deorientation takes place during the first shrinkage process, it should shrink to l_2.

The first shrinkage, then, is what the fibre experiences in the relaxer, and the second shrinkage is the residual shrinkage

in the relaxed product. To some degree PET follows these assumptions so it is possible to estimate relaxed product shrinkage from the dry heat shrinkage of drawn ribbons.

To do this what must be calculated is the shrinkage when the product shrunk at T_1 is shrunk a second time at T_2. This can be done by the using the definition of shrinkage and Figure 3 as follows:

$$\Phi_{ps} = (\%\ \text{shrinkage of sample shrunk at } T_1 \text{ when shrunk at } T_2) \ / \ 100 \qquad (5)$$

$$\Phi_{ps} = (l_1 - l_2) \ / \ l_1 = 1 - l_2 \ / \ l_1 \qquad (6)$$

If equations 3 and 4 are used to eliminate l_1 and l_2 in terms of the measured dry heat shrinkages at the two different temperatures this leads to:

$$\Phi ps = 1 - (1 - \Phi_2) \ / \ (1 - \Phi_1) \qquad (7)$$

From this, and the measured shrinkages, the expected product shrinkage at T_2 after an oven relaxation at T_1 can be calculated.

Figure 13 is a plot of predicted shrinkage for the technical useful case of high orientation, and high bath temperature. It appears that the predicted fibre shrinkages after a given oven relaxation are much too low. This indicates that significant crystalline change in addition to simple deorientation occurs in the drier/relaxer.

Example 3: Evaluation of PTT Staple Fiber Heat Setting on the Properties on PTT Spun Yarn Properties under Heated Strain Conditions: Yarns Evaluated included PTT, PTT/PET Blend, PTT/Cotton Blend, and PET (Table IV)

Breakage of filaments during the extrusion of PTT synthetic fibres severely limits production productivity and product quality. PTT resins with IV in the range of 0.55-1.0 are preferred, more preferably those with IV range of 0.675-0.92, and most preferably those with IV range of 0.72-0.82. Producing PTT synthetic fibres with an intrinsic viscosity range of 0.72-0.82 helps improve synthetic fibre production operability and product quality without a significant reduction in final fibre properties.

Reducing the intrinsic viscosity of PTT helps:

1. Reduce the amount of change in the viscosity of the chip compared to the viscosity of the extruded fibre.

2. Improve the homogeneity of polymer melt in the spin pack. PTT resin with 0.92 IV requires more severe spin pack filtration systems to maintain marginal yields in extrusion.

3. Improve production operability by decreasing the number of broken filaments during production.

4. Allow one to run the product with cooler extrusion temperatures for extruded filaments having less than 2-denier per filament. PTT is known to degrade at melt extrusion temperature above 260°C. When producing fine denier synthetic filament (filaments with less than 2 dpf) using 0.92 IV resin one has to increase the melt extrusion temperature to reduce the melt viscosity enough to avoid excessive melt flow turbulence and melt degradation which cause filaments to break during extrusion.

5. Reduce the amount of shrinkage in the product fibre making it easier to draw process and/or wind on to stable yarn packages.

Staple yarns made from PTT are surprisingly elastic - having recoverable elasticity when extended up to 15-25% of the original yarn length. This elasticity is also present in staple yarns produced from intimate and non-intimate fibre blends where PTT is the major fibre component by weight and/or length. Further, this elasticity is recoverable after several hundred cycles. The elasticity is sufficient enough to enhance the shape retention characteristics of textile fabrics produced from PTT staple yarns and blended staple yarns. Properly constructed and finished fabrics that contain a majority of PTT staple spun yarn (by weight of length percent) can have surprisingly high elastic recovery in woven and knit fabrics (tested with over 500 cycles by hand and 200 by instrument). The present invention covers the formation of staple spun yarns by conversion of staple into a twisted yarn structure by any method. The spun yarn can be made by hand, spinning wheel, ring-spinning, open-end spinning, air-jet spinning or other types of staple to yarn conversion equipment.

Staple yarns made from cotton, wool, acrylic, PET are not elastic. In order to produce staple yarns from these fibres that are elastic the industry commonly has to add an elastic continuous filament either internally to the yarn or fabric to give the final textile product elastic properties. These solutions are more expensive than a basic staple spun yarn made from PTT. The value of the present invention is that people with basic staple spun yarn technologies can produce an elastic spun yarn of commercial value without investing in more expensive core spun yarn equipment or incorporating elastic continuous filaments into the fabric structures, which then complicates how the fabric is dyed and finished.

An effort was made to briefly characterize how staple fiber heat setting properties impacts the behavior of yarns made from PTT staple and PTT staple blended with cotton, and PTT staple blended with PET staple. As noted in Table IV, the PET and

cotton blend yarn were prepared from several PTT staple supplies produced with differing relaxer temperature and having significantly different crimp. So, the effect of blending with other fibers cannot be definitely ascertained. Caution should therefore be used in inferring precise blend level effects from these experiments. This experiment looks at each of the example yarns in terms of shrinkage, modulus, stress decay and recovery. These factors are generally independent and were studied separately in this work.

Table IV: Fiber Properties

Item Number	PTT5-CR1-2	PTT5-CR1-3	PTT-CR1-4
Fiber Relaxation Oven Temp °C	105	120	135
Fiber Denier/Filament	1.75	1.80	1.79
Tenacity, cN/dtex	3.52	3.49	3.24
Elongation to Break, %	48	45	44
Load at 10% Strain, cN/dtex	0.83	1.21	1.13
Hand Crimp Index, %	28	19	18.5
Crimp/inch	14.8	15.8	14.2
Yarn Produced	100% PTT	50%PTT and 50% Cotton	50% PTT and 50%PET

Summary and Conclusions

For Spun Yarn 175°C Dry Heat Shrinkage:

- Spun yarn dry heat shrinkage decreased with oven temperature for all blends tested (100% PTT, 100% PET, 50/50 PTT/PET, and 50/50 PTT/Cotton).
- Dry heat shrinkage increases approximately ½% for each % applied stretch (or relaxation) for all blends tested.

- PTT spun yarn shrinkage was 2 to 2 ½ % less than PET yarns.
- PTT data closely followed the amorphous deorientation model for shrinkage.

- For Spun Yarn Boil off Shrinkage:
- Boil off shrinkage decreased with oven temperature for all blends tested.
- Boil off shrinkage increases about 0.4% for each 1% applied stretch for all blends tested.
- PTT spun yarns were about 1% lower than PET yarns in boil off shrinkage, because they were made by the draw relax process whereas the PET sample was draw anneal.

For Spun Yarn Load at 5% Strain (Stretch):

Fabrics are perceived as "stretchy" when very little force is required to change their length a significant amount. In this set of trials we choose to characterize stretch by observing the force required to strain the fabric 5%. The major variable affecting all blends tested was applied stretch. Oven temperature was much less important, this evaluation indicates:

- PTT exhibited 3-4 times less force to elongate 5% (greater stretch) than PET.
- The amount PTT's stretch decreases with applied stretch is $1/10^{th}$ that of PET (0.01 gpd increase/1% stretch vs 0.1) Therefore applied stretch can be used for PTT to modify yarn properties without a large yarn stretch penalty.
- The stretch of 100% PTT yarn was relatively insensitive to heat set conditions.

Spun Yarn Stress Decay

How much a yarn or fabric will recover after being subjected to a given strain for a given length of time depends on two factors:

1. How much stress decay occurs while the strain is maintained.
2. The amount of recovery after the strain is released.

These factors are generally independent and were studied separately in this work:

- PTT stress decay was independent of heat set temperature and decreased linearly with increasing applied stretch (0.5% reduction in stress decay / 1% applied stretch in heat setting).
- PET stress decay decreased with increasing oven temperature and linearly with increasing applied stretch. The applied stretch effect is considerably stronger than with PTT (-0.9% per % applied stretch).
- PTT and PET exhibited roughly the same amount of stress decay.
- PTT / PET blend yarns behaved about half way between the corresponding pure yarns with a -0.7% decrease per % applied stretch.
- PTT / Cotton blend yarn stress decay was independent of heat setting conditions.

Spun Yarn Recovery

Recovery for the PTT yarns from this sample set was much less than that observed for the pre-commercial yarn sample recently tested having 98% recovery. The cause for this may be

the 100°C drier oven used in fiber processing. The principal heat set variable affecting recovery for all samples tested was applied stretch, with increasing applied stretch increasing recovery:

- PTT recovery increases 0.9% per 1% applied stretch
- PTT generally had 5 to 10% higher recovery than PET
- PTT / Cotton blend data was very erratic but exhibited the same general trends as the pure yarns.

Shrinkage Fundamentals

In a semi crystalline polymer fiber with significant orientation, the orientation resides in two areas, the crystalline areas, and the amorphous areas connecting the crystalline domains. There is usually a range of crystal sizes, and the orientation of crystalline regions can vary.

When a fiber is exposed to temperatures below the glass transition temperature, length change is very slow and is called creep. In general, useful textile fibers all have low rates of creep in the absence of load. When the fiber is heated to temperatures above Tg, the amorphous areas become mobile and in the absence of a restraining force, deorient as closely as they can to the isotropic state (no preferential orientation). The isotropic state is favored by the second law of thermodynamics. This usually results in shrinkage, but in rare instances the crystalline regions are collapsed upon themselves and there is "negative" orientation so the fiber grows. Such fibers are called self elongatable. It is not known if they can be made from PTT. The crystalline regions are not mobile, and do not deorient.

As one continues to increase the temperature of the fiber, smaller crystals melt and their domain becomes amorphous. They now deorient and additional shrinkage occurs. This is why shrinkage generally increases with temperature for a semi

crystalline polymer. So there are two strategies for reducing fiber shrinkage:

1. Preshrink to the temperature at which you want the fiber to be stable

2. Crystallize under heat and tension at a temperature which yields crystals stable at the temperature at which you do not want the fiber to shrink.

For commodity PET fiber, where the issues are spinning and weaving efficiency and yarn strength, the second route is exclusively used, because as we will see later, preshrinking reduces fiber modulus. Specialty fibers, particularly for wool blends, use the first route because strength and modulus are not important issues, but the better dyeability offered by route 1 is an advantage. At this juncture, it is not clear which is the better route for PTT.

If a fiber is stretched, its amorphous orientation increases, and so does shrinkage. In PET untwisted continuous filament yarn there is often nearly a 1 to 1 correspondence (5% stretch increases shrinkage 5%).

So far we have been discussed single uncrimped fibers. The situation for spun yarn is more complex because:

- Fibers are twisted at a helix angle which reduces the effect of fiber shrinkage on the yarn
- Fibers migrate from outside to the middle of the yarn
- Fibers can slip in the yarn
- The presence of blend fibers with different shrinkages can change the shrinkage of the assembly.

Even with these complexities, we can use the simple model to predict responses of a spun yarn to heat setting conditions:

1. If the yarn is heated and allowed to free relax, it should deorient and crystallinity should increase. Both factors decrease shrinkage. At a constant oven temperature, the shrinkage decrease should be linear with the relaxation. Shrinkage should decrease with increasing oven temperature.

2. If a yarn is heated and held at constant length there is no deorientation. Shrinkage decreases with increasing oven temperature as long as the yarn treatment oven temperature is higher than the fiber experienced during the free to relax step in fiber manufacture.

3. If a yarn is heated and stretched, orientation increases and therefore so should shrinkage. Shrinkage should increase linearly with applied stretch, and decrease with increasing oven temperature, providing that it is higher than that seen during fiber processing.

With this foundation in place, we are now ready to analyze the effect of heat setting conditions on yarn shrinkage.

175 °C Spun Yarn Dry Heat Shrinkage

As illustrated in Figure 14, PTT is a wonderful substrate that follows all the rules of the total orientation model.

At 0% applied stretch the control which was relaxed at 100°C has exactly the same shrinkage as the yarn treated at 100°C. When treated at higher temperatures, still at constant length, the shrinkage decreases.

As length is changed by applied stretch, or shrinkage, the shrinkage increases linearly with applied stretch, and the slopes are roughly constant with oven temperature. At a given oven temperature 176°C dry heat shrinkage increases about 0.46% per 1% applied stretch.

PET behaves in a similar manner, Figure 15. Because it is an annealed, and not a relaxed fiber, shrinkage of the control yarn decreases with increasing oven temperature even at 100°C. Because it is high modulus, at high stretch and low oven temperature the fibers do not stretch, but slip in the yarns so the shrinkage increase is not so great as for PTT. For oven temperatures above 130°C PET dry heat shrinkage increases about 0.55% per 1% applied stretch. This is somewhat higher that PTT, but a good rule of thumb for both is ½% shrinkage increase for each % stretch.

Figure 16 compares PTT and PET yarn shrinkage for the highest and lowest heat set temperatures. PTT has about 2 to 2 ½% lower dry heat shrinkage than PET for equivalent oven conditions. As mentioned above both have roughly the same increase in shrinkage with applied stretch.

The PTT / Cotton blend is similar to the PET blend (Figure 17) with shrinkage increasing with decreased oven temperature and increasing applied stretch. The increase with applied stretch is fairly linear and shrinkage increases roughly 0.47 % per 1% applied stretch. Shrinkage of the cotton blends is approximately 1% less than the PET blend for similar conditions. For this sample set a good rule of thumb is that 1% applied stretch increases dry heat shrinkage ½ %.

Spun Yarn Boil Off Shrinkage

Boil off shrinkage behaves in the same way as dry heat, except that the amorphous orientation available is that present

in the fiber plus all crystals which melt between the glass transition and 100°C, so it is much less than the dry heat shrinkage. In some fibers where the plastization effect of water is high, this shrinkage can be considerable. Fibers produce by a draw relax process with relaxation temperatures above 100°C generally have very low boil off shrinkages. Annealed fibers generally have relatively high boil off shrinkage because they are heated under tension and there is always amorphous orientation present.

These samples in general followed these principles. All blends behaved in a manner similar to dry heat shrinkage with shrinkage decreasing with increasing oven temperature, and increasing with applied stretch.

The PTT control yarn had a shrinkage of 2% even though the fibers which went into it were oven relaxed at 100 C. This indicates that some cold drawing occurred in processing, probably during carding. This is not unexpected, given PTT's low modulus. PTT yarn shrinkage increased about 0.38% per 1% applied stretch. The control PET yarn had considerably higher shrinkage than PTT (4.5 vs 2%) because it is produced by the annealing process. Yarn shrinkage increased 0.47% per 1% applied stretch. In general PTT yarns have approximately 1% less dry heat shrinkage than PET yarns given similar yarn heat setting conditions (Figure 18).

The PTT/PET blend yarns had a shrinkage increase of 0.44% per 1% applied stretch, and the PTT/Cotton yarn hand an increase of 0.417. A good rule of thumb for boil off shrinkage is that it increases about 0.4% per 1% applied stretch for all conditions tested.

For 100% PTT spun yarns, load at 5% strain is nearly independent of oven temperature, and is linearly related to applied stretch increasing 0.01gpd per 1% increase in applied

stretch. This means that yarn stretch decreases as the yarn is drawn during heat setting. Note for the PTT data that the control yarn, which was produced from fibers relaxed at 100100% has essentially the same load at 5% strain as that heat set at 0 stretch and 100°C.

PET yarns behaved in a similar manner. In this case there was a considerable change for the control yarn vs yarn heat set at 100°C and 0 applied stretch because the feed fibers were annealed, not relaxed. PET load at 5% elongation increases an order of magnitude higher than PTT with applied stretch, 0.1 gpd/1% applied stretch.

Figure 19 compares the behavior of PTT and PET, and PTT's stretch advantage is strikingly apparent. Not only is the force required for 5% strain a factor of 3 lower with no applied stretch, the response to applied stretch is much less, which means applied stretch can be used in heat setting PTT yarns without paying an excessive price in yarn stretch. Interestingly the highest applied stretch PTT item (7.5%) requires 45% less force at 5% strain than a PET sample which is relaxed 7.5%.

Spun Yarn Stress Decay

How much strain a yarn or fabric will recover after being strained and held at constant length for a period of time depends on two factors:

How much stress decay occurs while the sample is held at constant length. In the extreme, if all the stress is lost, the recovery will be zero.

How much strain is recovered after the test time period.

This spun yarn stress decay experiment involved straining

the yarn 5%, then holding the spun yarn at length for 2 minutes and allowing the yarn to recover to zero stress. Stress decay was calculated manually from the test charts, and is somewhat less accurate than machine calculated numbers from computerized analysis methods. Stress decay and recovery are two separate phenomena and are discussed separately.

Stress decay of 100% PTT yarns was independent of oven temperature and decreased linearly with applied stretch. While intuitively it is believed stress decay should increase with applied stretch, the r2 for this correlation is quite high. PTT stress decay decreases about 0.5% per % applied stretch. PET yarn behaved in a similar way although there is a definite oven temperature effect, and the decrease per unit applied stretch (0.9% decay / 1% applied stretch) is nearly double that of PTT. Figure 20 compares PTT and PET stress decay. In general PET is higher at low applied stretch, and lower than PTT at high oven temperature and applied stretch. The behavior of the PTT / PET blend is half way between the two pure fibers with less oven temperature sensitivity and a 0.7% stress decay decrease per 1% applied stretch. Stress decay for the PTT / Cotton blends was independent of heat setting conditions.

Spun Yarn Recovery

PTT recovery was not affected by oven temperature and increased linearly with increasing applied stretch (0.9 % recovery per 1% applied stretch). PET recovery increased marginally with increase in oven temperature but the principal effect was applied stretch. Its response is much more pronounced than for PTT with an increase of 2.2 % recovery for each 1% applied stretch. As indicated in Figure 21, PTT generally has 5-10% higher recovery than PET except where PET has had high levels of applied stretch in a high temperature oven. The PTT / PET blend yarn responded like pure PTT with no oven temperature dependence and a strong response to applies

stretch (1.7% increase in recovery for each 1% applied stretch. PTT / Cotton blend results were erratic with both higher oven temper and higher applied stretch increasing recovery.

Property Trade Off in Spun Yarn Heat Setting

One of the primary reasons for doing this work is to answer the question: "If heat setting the yarn to reduce its shrinkage then how much does stretch, recovery and stress decay deteriorate?". To answer this question for this data set it is necessary to plot these variables against each other. Since all variables are dependent variables, the relationships hold true only for this data set and others in which the dependent variables were changed in the same manner as we did here. With this caveat let us observe the responses:

For the stretch / dry heat shrinkage tradeoff, stretch increases (load at 5% strain decreases) as dry heat shrinkage is decreased. This is a favorable trade since there is no stretch penalty to be paid by reducing shrinkage by letting the yarn shrink. Although the r2 is quite low at 0.47, considering that every point is included, this data is probably a reliable trend guide. Load at 5% decreases 0.01 gpd for each 1% reduction in shrinkage.

The recovery / dry heat shrinkage tradeoff is unfavorable. Recovery decreases 1.3% for each 1% reduction in dryheat shrinkage. r2 for this data was a respectable 0.64.

The stress decay / dry heat shrinkage tradeoff is unfavorable with stress decay increasing 0.9% for each 1% reduction in dry heat shrinkage. It is believed this increase in stress decay is responsible for the reduction in recovery. In any case dry heat shrinkage should only be reduced the minimal amount required by the end user.

Example 4: Lowering Resin PTT Resin IV from 0.92 to 0.82 Provides Improved Extrusion Reliability in PTT Staple Production

Breakage of filaments during the extrusion of PTT synthetic fibers severely limits production productivity and product quality. Producing PTT synthetic fibers with an intrinsic viscosity range of 0.72-0.82 helps improve synthetic fiber production operability and product quality without a significant reduction in final fiber properties.

Reducing the intrinsic viscosity of PTT helpsreduce the amount of change in the viscosity of the chip compared to the viscosity of the extruded fiber. It also improves the homogeneity of polymer melt in the spin pack. PTT resin with 0.92 IV requires more severe spin pack filtration systems to maintain marginal yields in extrusion. It also helps improve production operability by decreasing the number of broken filaments during production. It allows one to run the product with cooler extrusion temperatures for extruded filaments having less than 2-denier per filament. PTT is known to degrade at melt extrusion temperature above 260°C. When producing fine denier synthetic filament (filaments with less than 2 dpf) using 0.92 IV resin one has to increase the melt extrusion temperature to reduce the melt viscosity enough to avoid excessive melt flow turbulence and melt degradation that results in which cause filaments to break during extrusion. It also reduces the amount of shrinkage in the product fiber making it easier to draw process and/or wind onto stable yarn packages.

C L A I M S

1. A process for making textile staple fibre from polytrimethylene terephthalate (PTT) on existing PET textile staple fibre making equipment which comprises:

(a) melt extruding PTT polymer at 245 to 253° C,

(b) spinning the extruded PTT into yarn using at least one spinneret,

(c) moving the spun yarn to a first takeup roll wherein the distance from the spinneret to the first takeup roll is from 16 to 20 feet,

(d) cooling the spun yarn to less than 31°C before it reaches the first takeup roll,

(e) optionally, storing the spun yarn at a temperature of no more than 31°C,

(f) prior to the draw process, preconditioning the yarn under tension at a temperature of at least 60°C,

(g) drawing the yarn at a temperature of at least 60°C,

(h) optionally, allowing the drawn yarn to relax at a temperature of up to 190°C ,and

(i) crimping the drawn yarn at a temperature of 70 to 120°C and decreasing the drawn yarn feed rate by 10 to 60 percent by denier from the drawn yarn feed rate used for making comparable PET.

2. The process of claim 1 wherein the intrinsic viscosity of the PTT is from 0.55 to 1.0.

3. The process of claim 2 wherein the intrinsic viscosity of the PTT is from 0.72 to 0.82.

4. The process of claim 1, 2 or 3 wherein the spun yarn is cooled to less than 25°C before it reaches the first takeup roll.

5. The process of claim 1 wherein the relaxation step is not used and the crimping temperature is 70 to 100°C.

6. The process of claim 1 wherein the relaxation step is used and the crimping temperature is 80 to 120°C.

7. The process of any one of the preceding claims wherein step (i) further comprises using a crimper volume of 10 to 50 percent more than the crimper volume of the crimper used to make comparable PET.

8. The process of any one of the preceding claims wherein the drawn yarn feed rate is decreased by 40 to 60 percent.

9. A process for making textile staple fibre from polytrimethylene terephthalate (PTT) on existing PET textile staple fibre making equipment which comprises:

(a) melt extruding PTT polymer at 245 to 253° C,

(b) spinning the extruded PTT into yarn using at least one spinneret,

(c) moving the spun yarn to a first takeup roll wherein the distance from the spinneret to the first takeup roll is from 16 to 20 feet,

(d) cooling the spun yarn to less than 31°C before it reaches the first takeup roll,

(e) optionally, storing the spun yarn at a temperature of no more than 31°C,

(f) prior to the draw process, preconditioning the yarn under tension at a temperature of at least 60°C,

(g) drawing the yarn at a temperature of at least 60°C,

(h) optionally, allowing the drawn yarn to relax at a temperature of up to 190°C ,and

(i) crimping the drawn yarn at a temperature of 70 to 120°C and using a crimper volume of 10 to 50 percent more than the crimper volume of crimper used to make comparable PET.

10. The process of any one of the preceding claims wherein step (g) involves at least two draws, the first carried out at least 60°C and the second and subsequent draws, if any, carried out at a higher temperature than the first up to the melting point of the yarn.

Figure 1

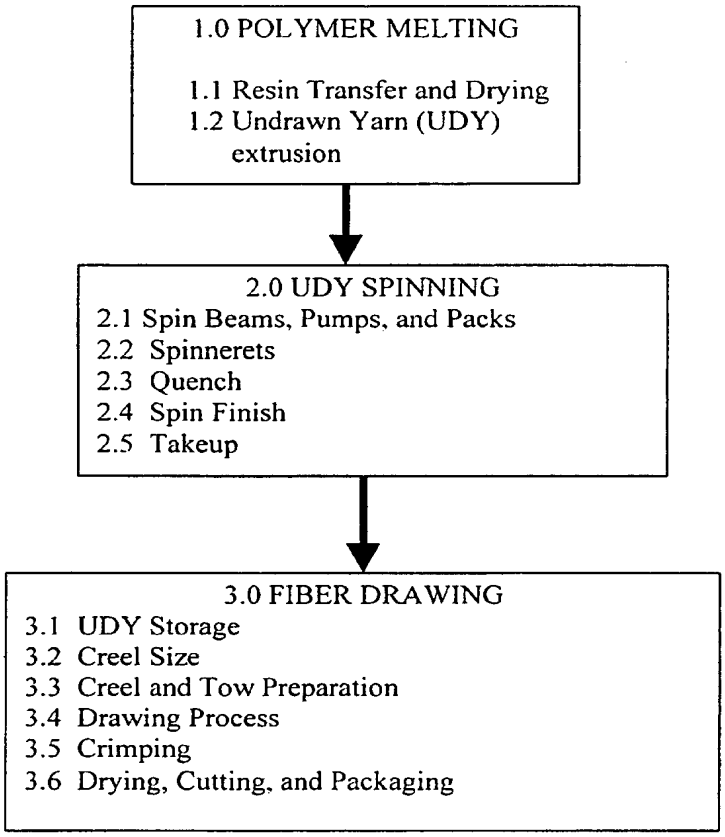


Figure 2

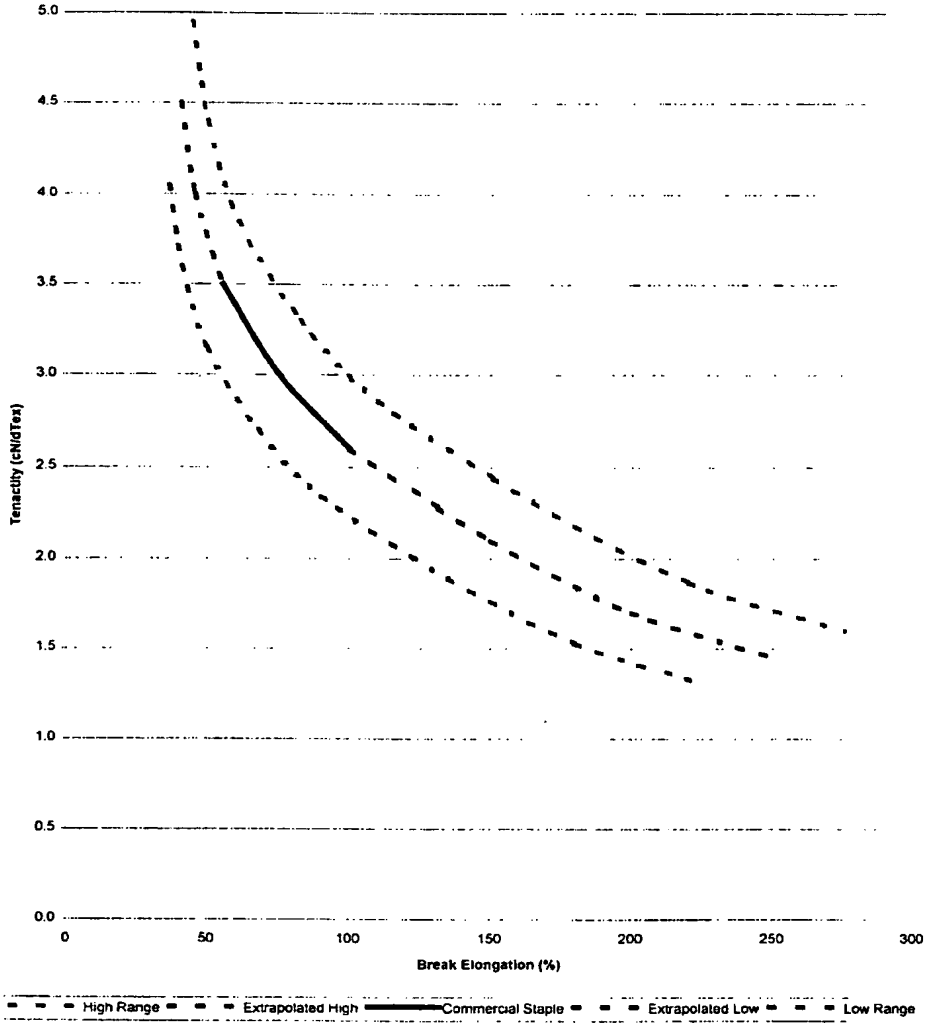

5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Tenacity (cN/dTex)
0
50
100
150
200
250
300
Break Elongation (%)
High Range
Extrapolated High
Commercial Staple
Extrapolated Low
Low Range

Figure 3

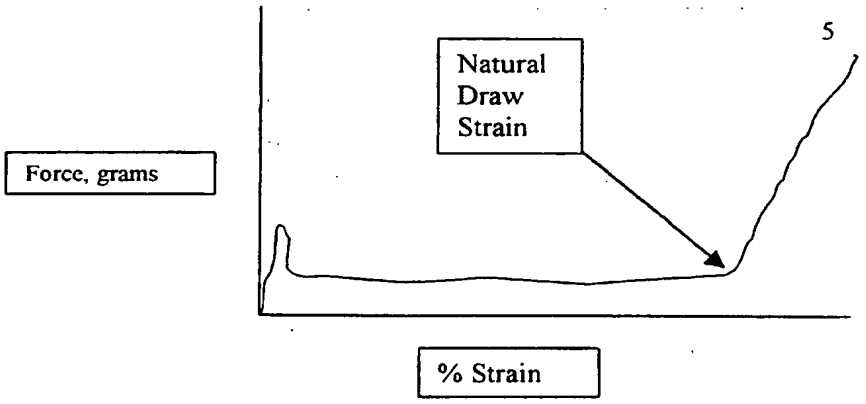


Figure 4

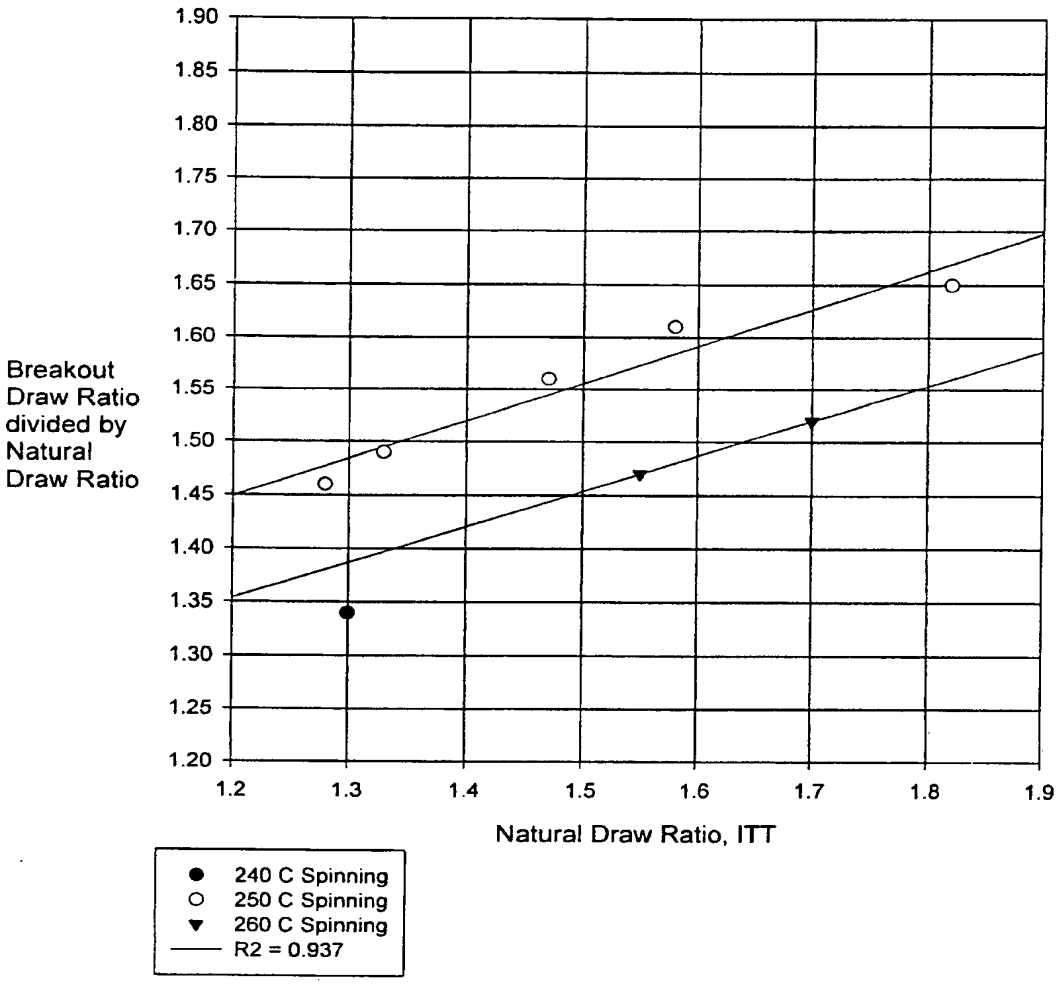

Breakout Draw Ratio divided by Natural Draw Ratio
1.90
1.85
1.80
1.75
1.70
1.65
1.60
1.55
1.50
1.45
1.40
1.35
1.30
1.25
1.20
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
Natural Draw Ratio, ITT
240 C Spinning
250 C Spinning
260 C Spinning
R2 = 0.937

Figure 5

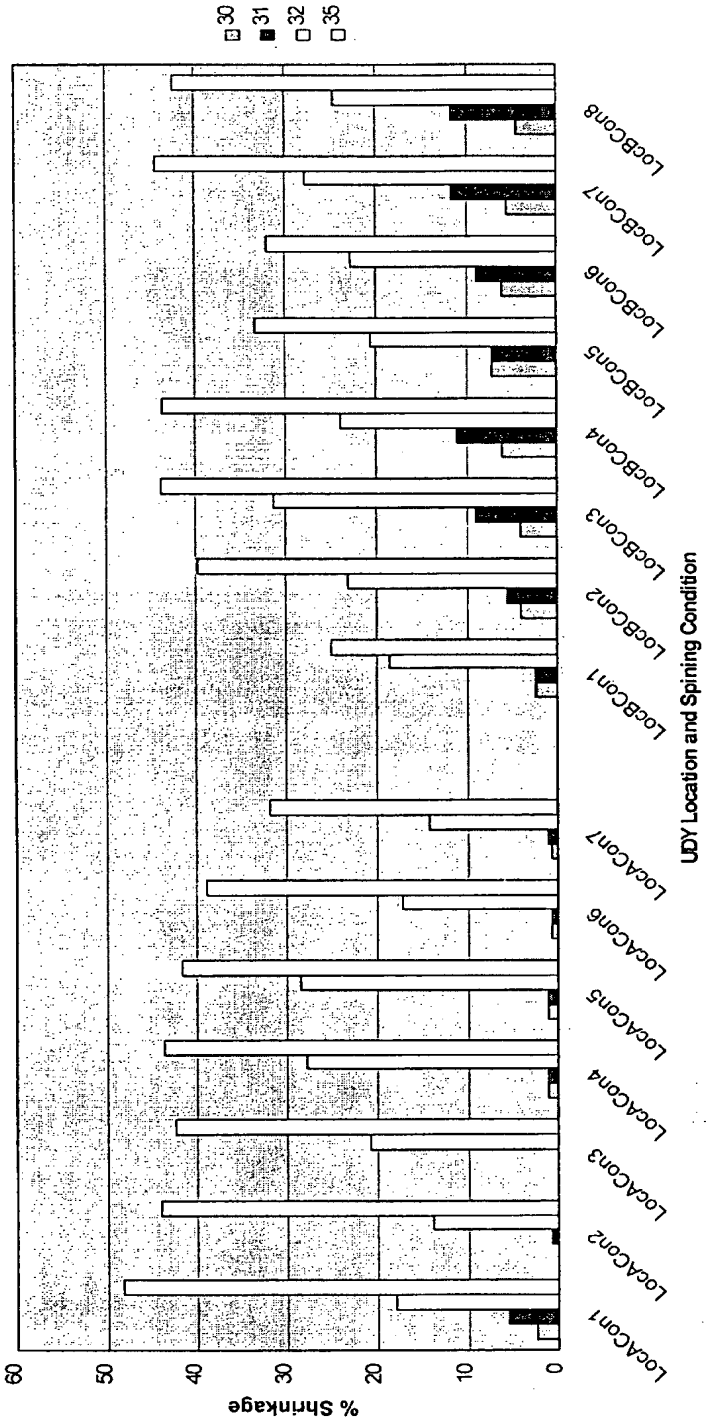

30
31
32
35
% Shrinkage
60
50
40
30
20
10
0
LocACon1
LocACon2
LocACon3
LocACon4
LocACon5
LocACon6
LocACon7
LocBCon1
LocBCon2
LocBCon3
LocBCon4
LocBCon5
LocBCon6
LocBCon7
LocBCon8
UDY Location and Spining Condition

Figure 6

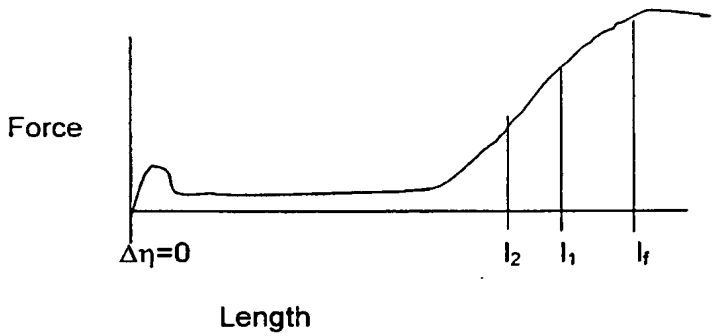


Figure 7

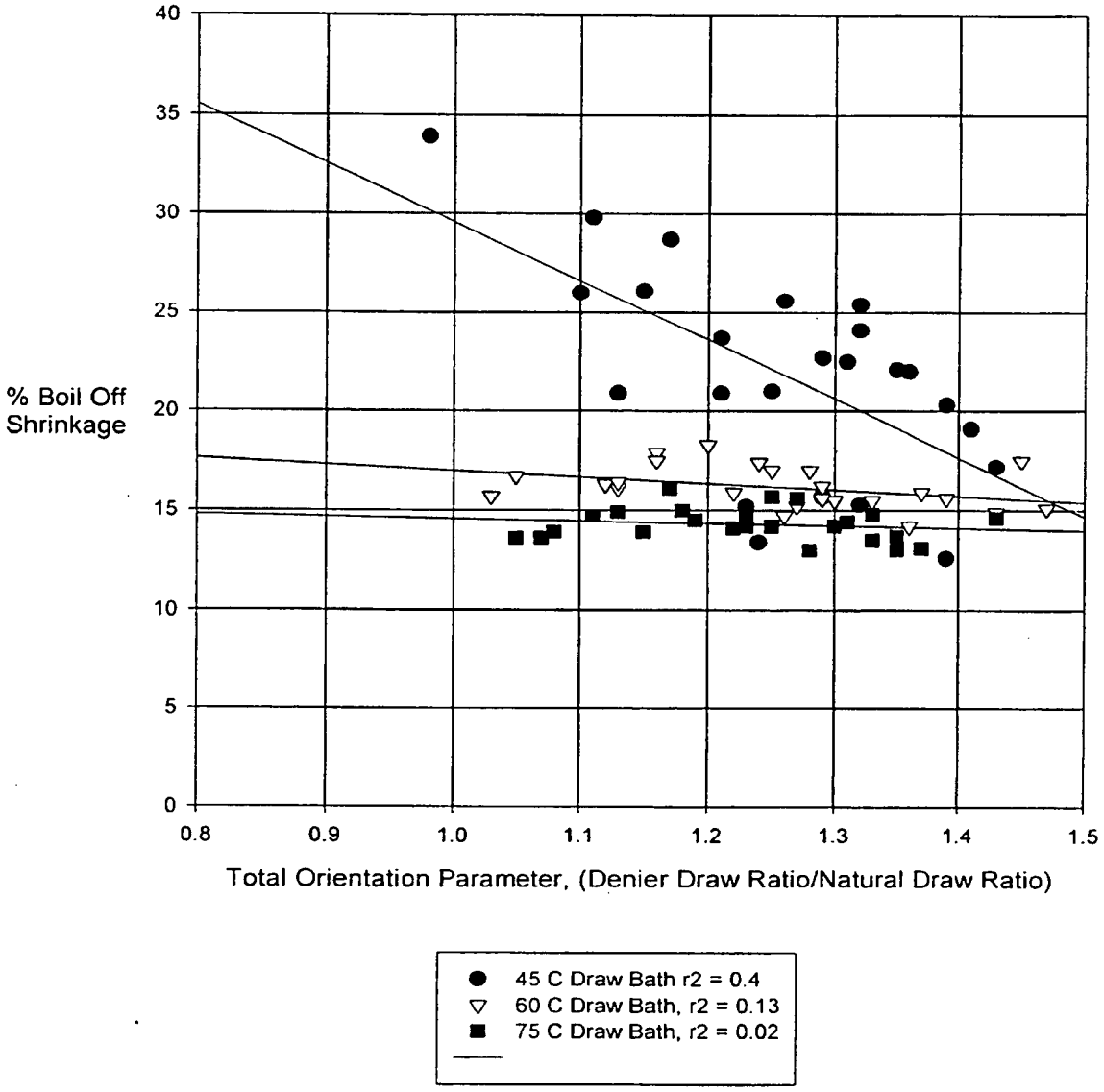

40
35
30
25
20
15
10
5
0
% Boil Off Shrinkage
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
Total Orientation Parameter, (Denier Draw Ratio/Natural Draw Ratio)
45 C Draw Bath r2 = 0.4
60 C Draw Bath, r2 = 0.13
75 C Draw Bath, r2 = 0.02

Figure 8

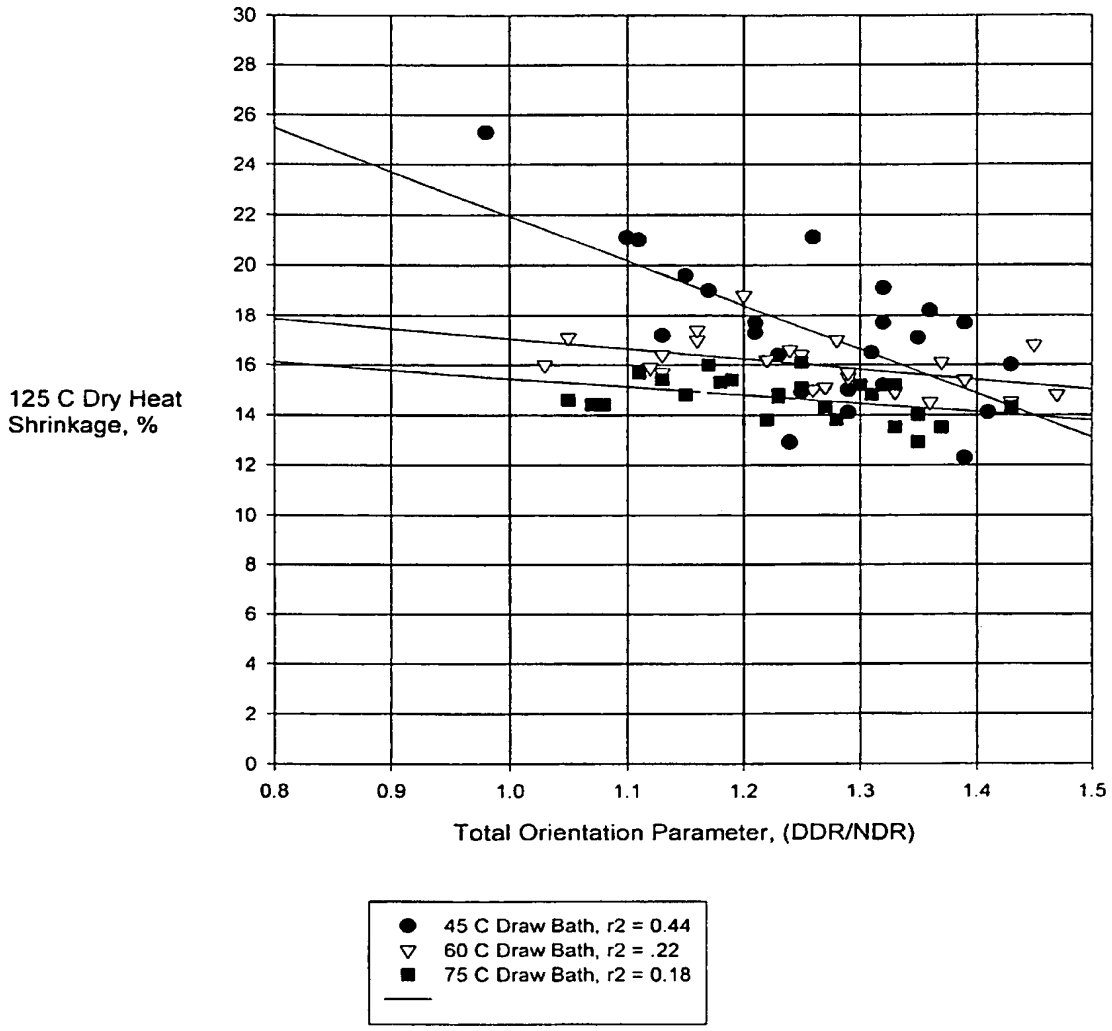

125 C Dry Heat Shrinkage, %
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
Total Orientation Parameter, (DDR/NDR)
45 C Draw Bath, r2 = 0.44
60 C Draw Bath, r2 = .22
75 C Draw Bath, r2 = 0.18

Figure 9

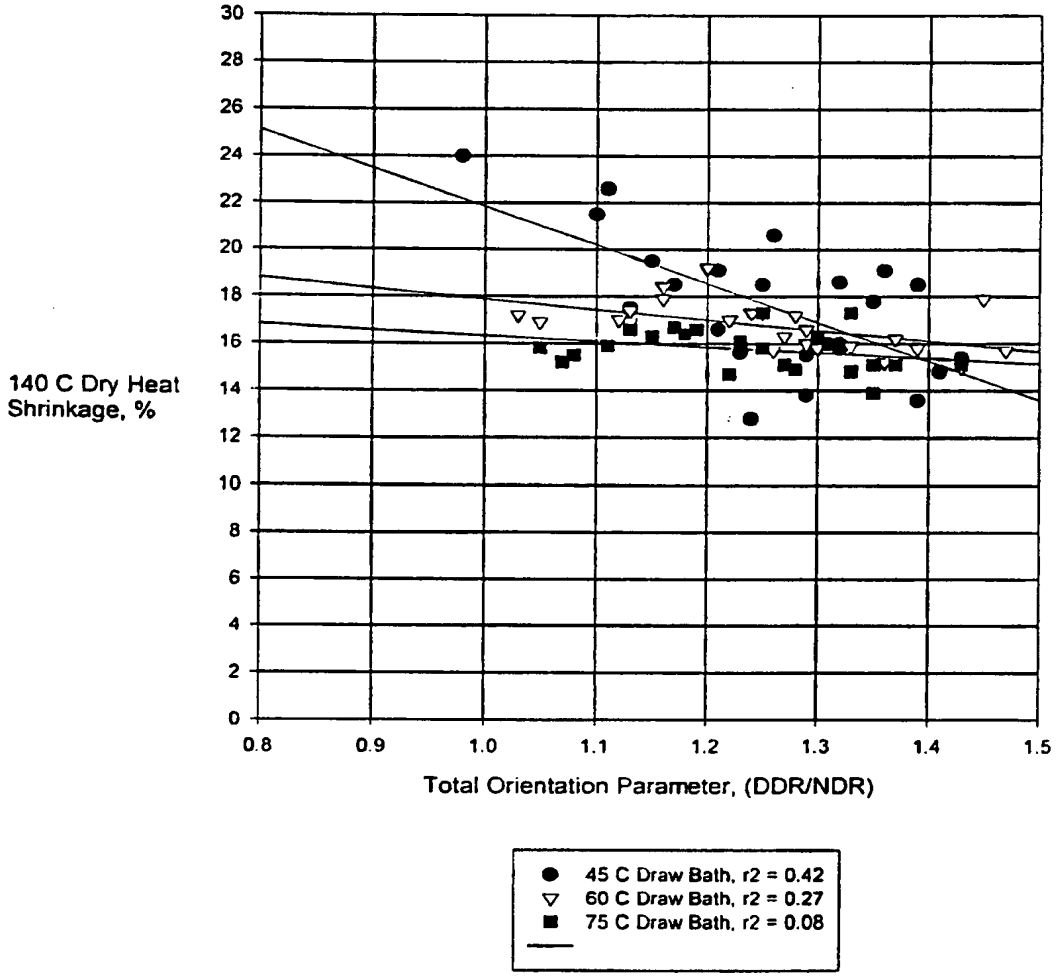

140 C Dry Heat Shrinkage, %
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
Total Orientation Parameter, (DDR/NDR)
45 C Draw Bath, r2 = 0.42
60 C Draw Bath, r2 = 0.27
75 C Draw Bath, r2 = 0.08

Figure 10

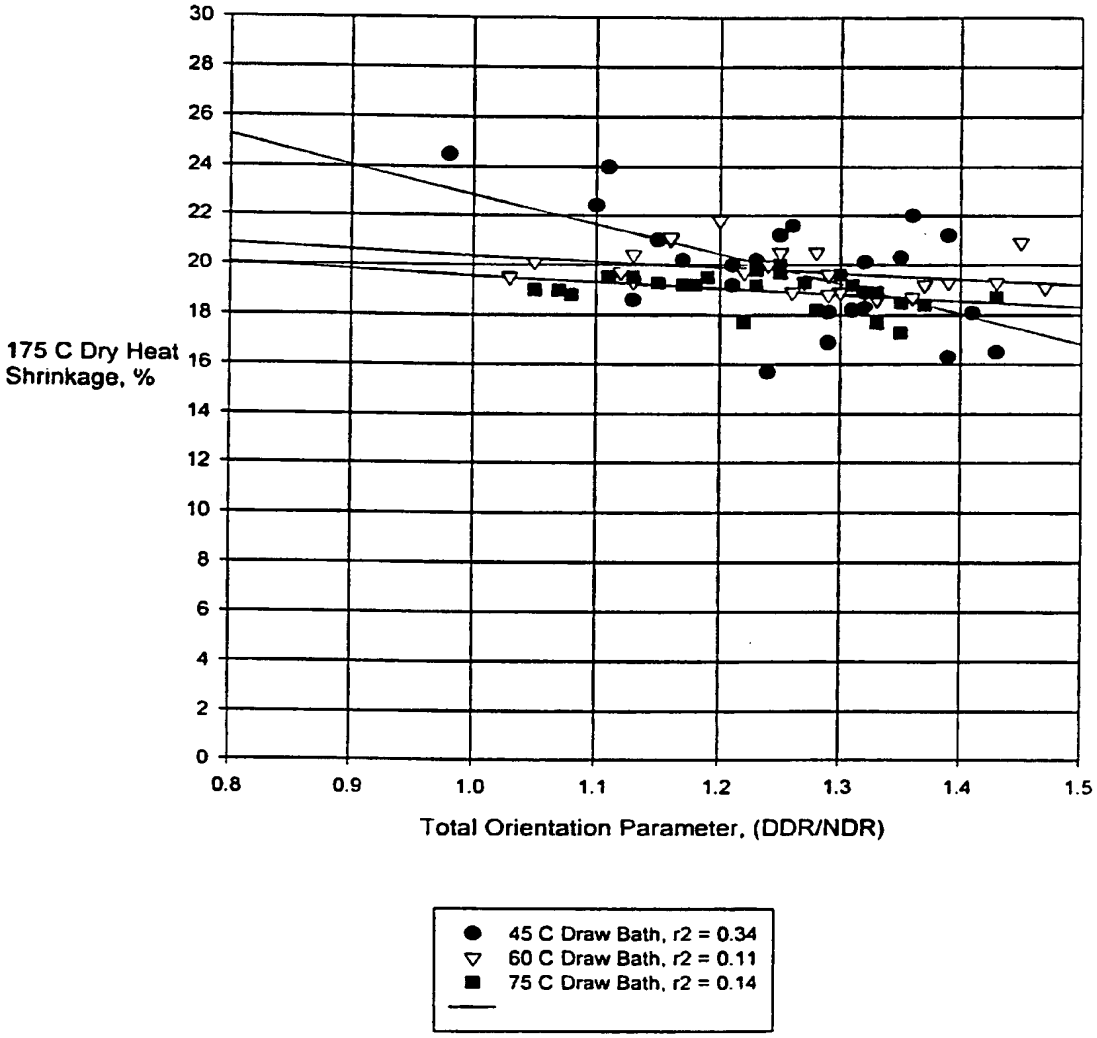

175 C Dry Heat Shrinkage, %
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
Total Orientation Parameter, (DDR/NDR)
45 C Draw Bath, r2 = 0.34
60 C Draw Bath, r2 = 0.11
75 C Draw Bath, r2 = 0.14

Figure 11

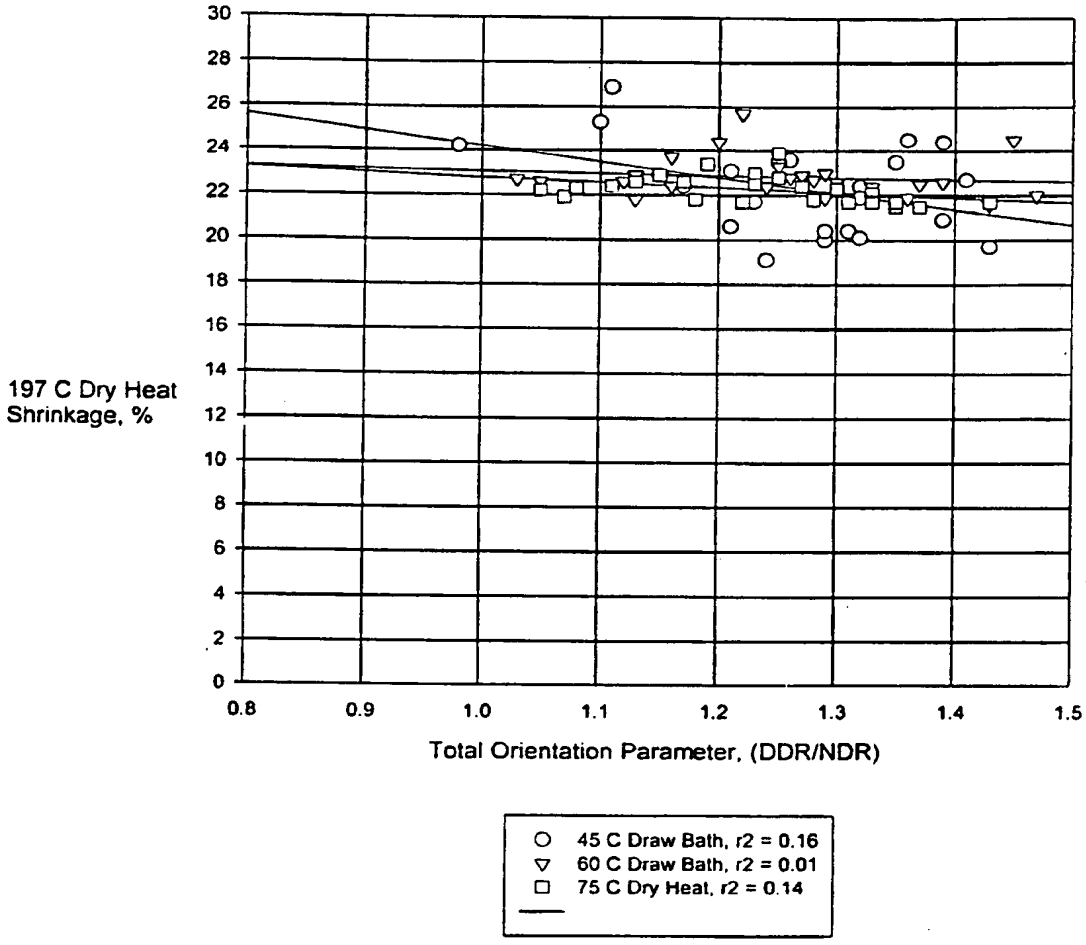

197 C Dry Heat Shrinkage, %
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
Total Orientation Parameter, (DDR/NDR)
45 C Draw Bath, r2 = 0.16
60 C Draw Bath, r2 = 0.01
75 C Dry Heat, r2 = 0.14

Figure 12

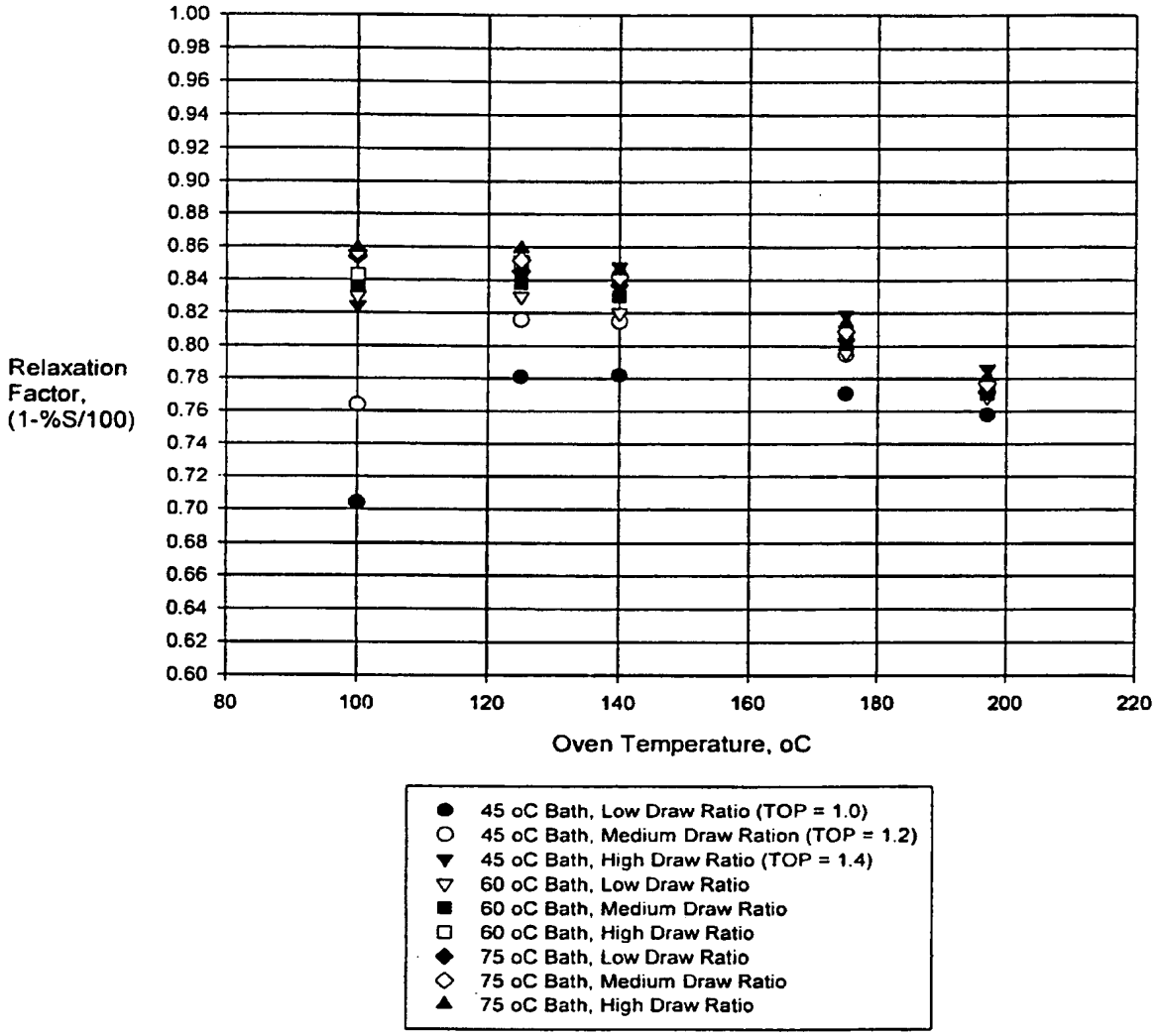

Relaxation Factor, (1-%S/100)
1.00
0.98
0.96
0.94
0.92
0.90
0.88
0.86
0.84
0.82
0.80
0.78
0.76
0.74
0.72
0.70
0.68
0.66
0.64
0.62
0.60
80
100
120
140
160
180
200
220
Oven Temperature, oC
45 oC Bath, Low Draw Ratio (TOP = 1.0)
45 oC Bath, Medium Draw Ration (TOP = 1.2)
45 oC Bath, High Draw Ratio (TOP = 1.4)
60 oC Bath, Low Draw Ratio
60 oC Bath, Medium Draw Ratio
60 oC Bath, High Draw Ratio
75 oC Bath, Low Draw Ratio
75 oC Bath, Medium Draw Ratio
75 oC Bath, High Draw Ratio

Figure 13

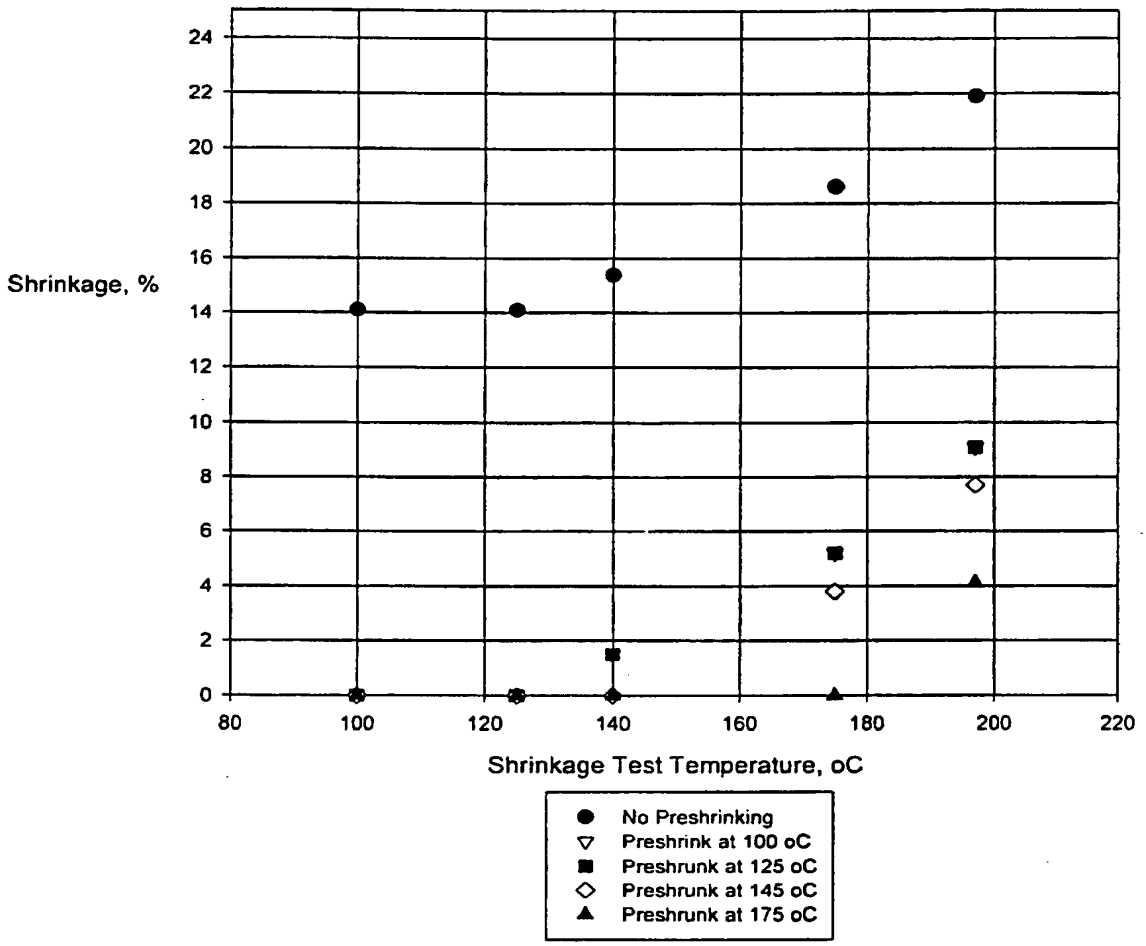

Shrinkage, %
24
22
20
18
16
14
12
10
8
6
4
2
0
80
100
120
140
160
180
200
220
Shrinkage Test Temperature, oC
No Preshrinking
Preshrink at 100 oC
Preshrunk at 125 oC
Preshrunk at 145 oC
Preshrunk at 175 oC

Figure 14

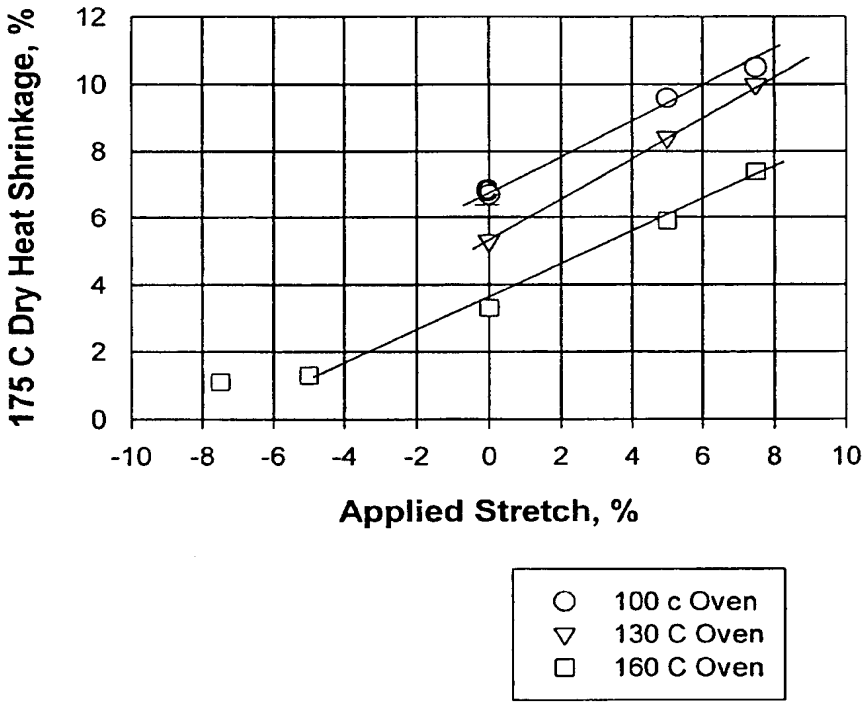

175 C Dry Heat Shrinkage, %
12
10
8
6
4
2
0
-10
-8
-6
-4
-2
0
2
4
6
8
10
Applied Stretch, %
100 c Oven
130 C Oven
160 C Oven

Figure 15

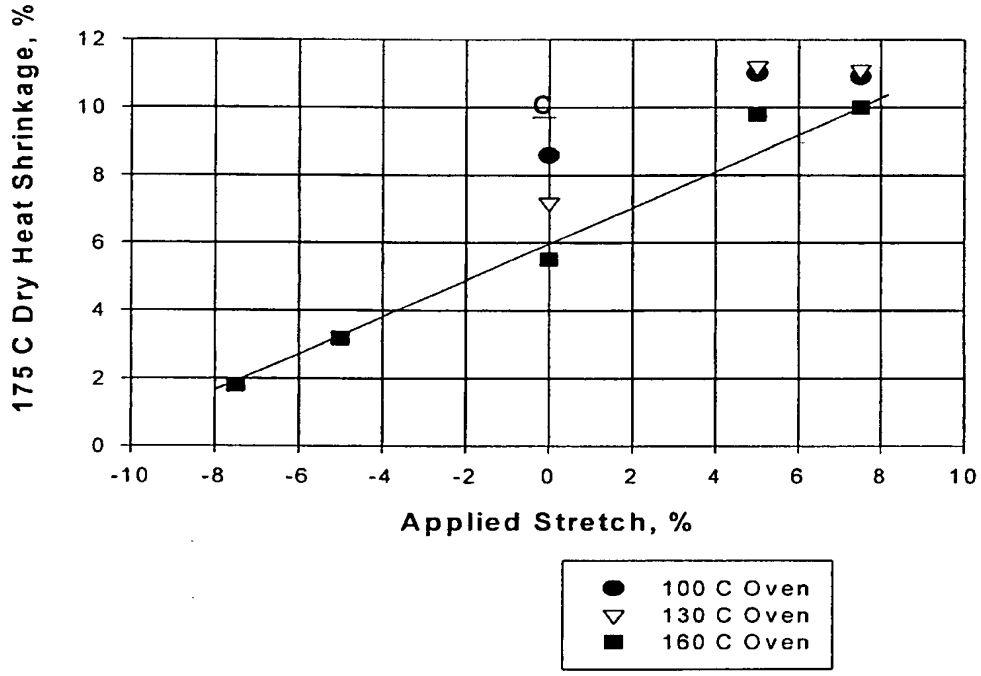

175 C Dry Heat Shrinkage, %
12
10
8
6
4
2
0
-10
-8
-6
-4
-2
0
2
4
6
8
10
C
Applied Stretch, %
100 C Oven
130 C Oven
160 C Oven

Figure 16

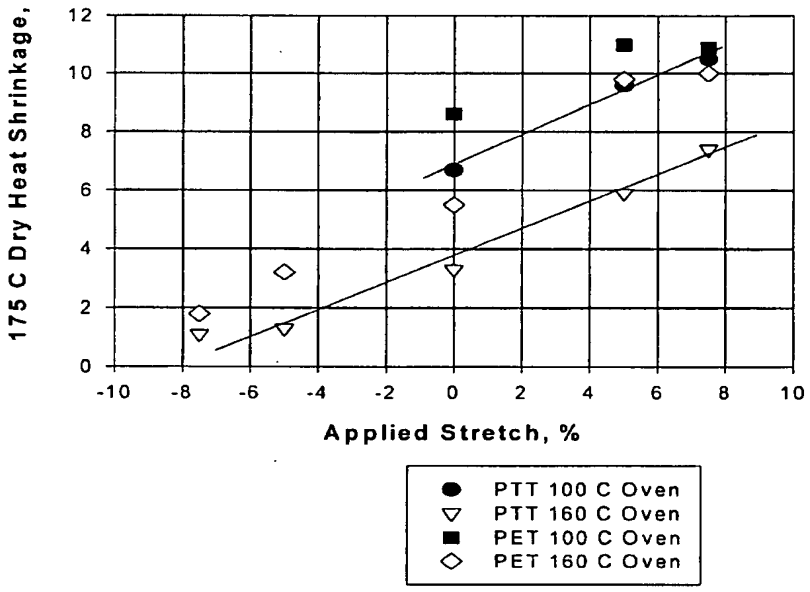

175 C Dry Heat Shrinkage,
12
10
8
6
4
2
0
-10
-8
-6
-4
-2
0
2
4
6
8
10
Applied Stretch, %
PTT 100 C Oven
PTT 160 C Oven
PET 100 C Oven
PET 160 C Oven

Figure 17

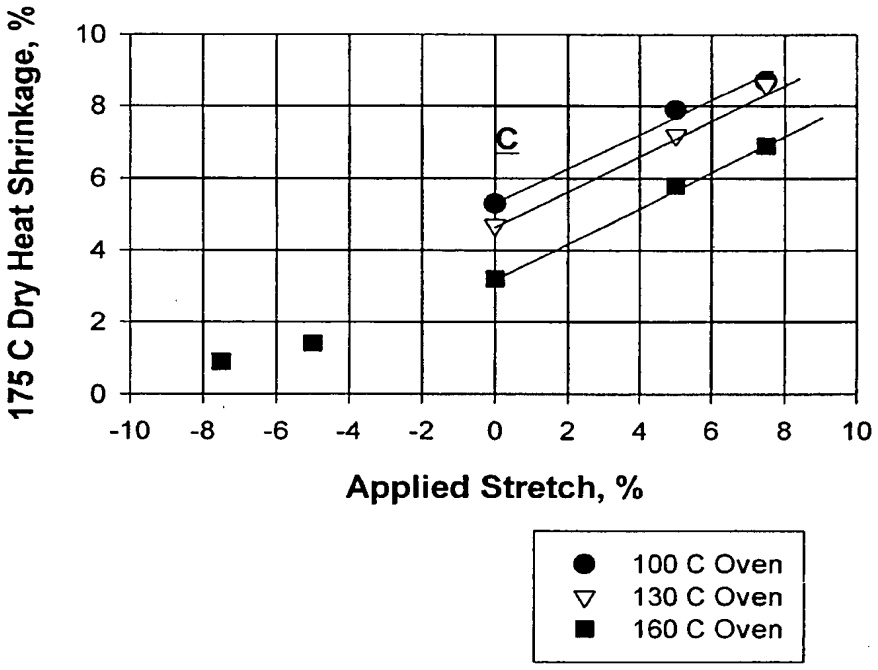

175 C Dry Heat Shrinkage, %
10
8
6
4
2
0
-10
-8
-6
-4
-2
0
2
4
6
8
10
C
Applied Stretch, %
100 C Oven
130 C Oven
160 C Oven

Figure 18

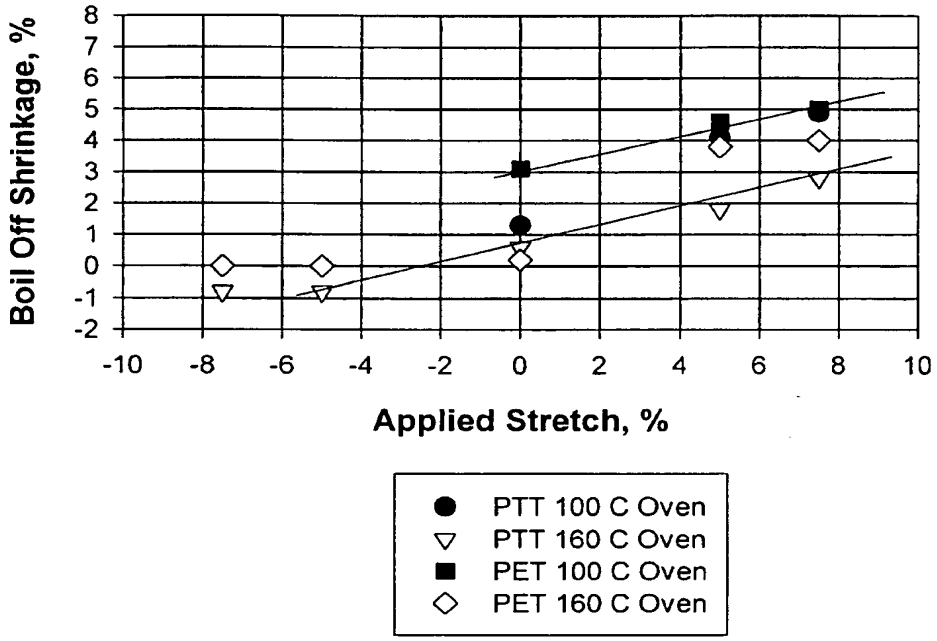

Boil Off Shrinkage, %
8
7
6
5
4
3
2
1
0
-1
-2
-10
-8
-6
-4
-2
0
2
4
6
8
10
Applied Stretch, %
PTT 100 C Oven
PTT 160 C Oven
PET 100 C Oven
PET 160 C Oven

Figure 19

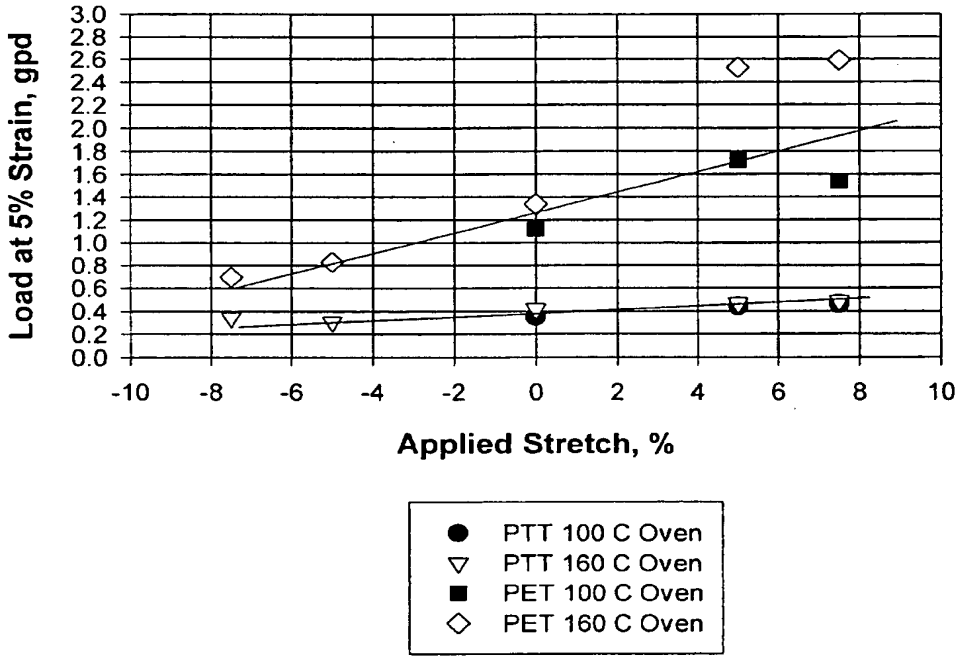

Load at 5% Strain, gpd
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-10
-8
-6
-4
-2
0
2
4
6
8
10
Applied Stretch, %
PTT 100 C Oven
PTT 160 C Oven
PET 100 C Oven
PET 160 C Oven

Figure 20

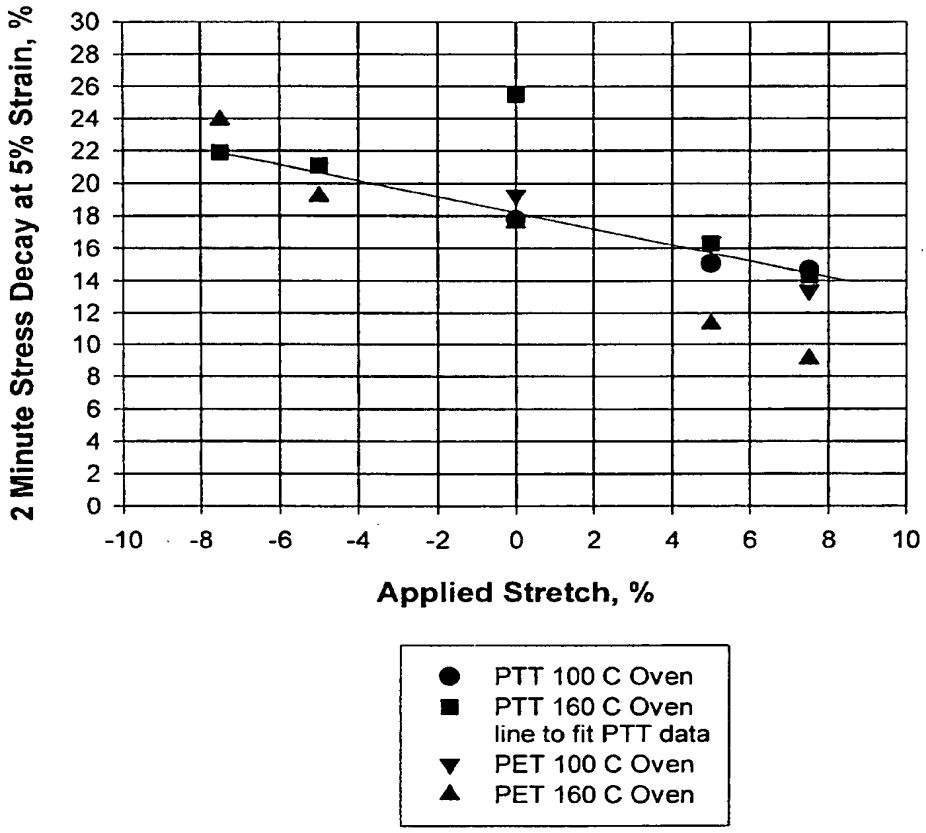
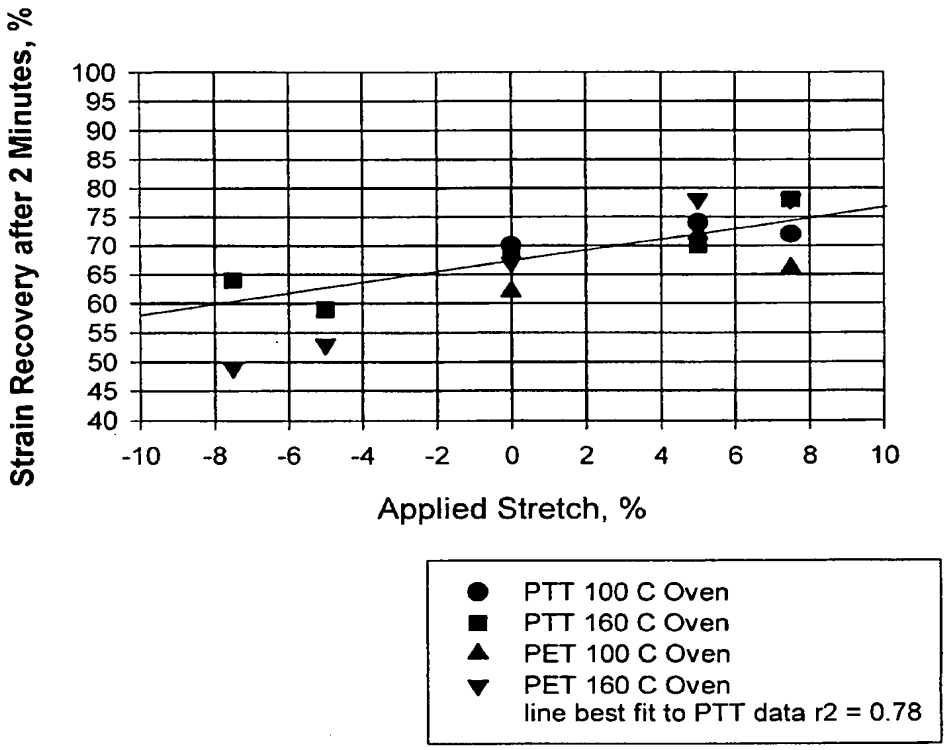

2 Minute Stress Decay at 5% Strain, %
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
-10
-8
-6
-4
-2
0
2
4
6
8
10
Applied Stretch, %
PTT 100 C Oven
PTT 160 C Oven
line to fit PTT data
PET 100 C Oven
PET 160 C Oven

Figure 21


Strain Recovery after 2 Minutes, %
100
95
90
85
80
75
70
65
60
55
50
45
40
-10
-8
-6
-4
-2
0
2
4
6
8
10
Applied Stretch, %
PTT 100 C Oven
PTT 160 C Oven
PET 100 C Oven
PET 160 C Oven
line best fit to PTT data r2 = 0.78

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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60/189,531 15 March 2000 (15.03.2000) US

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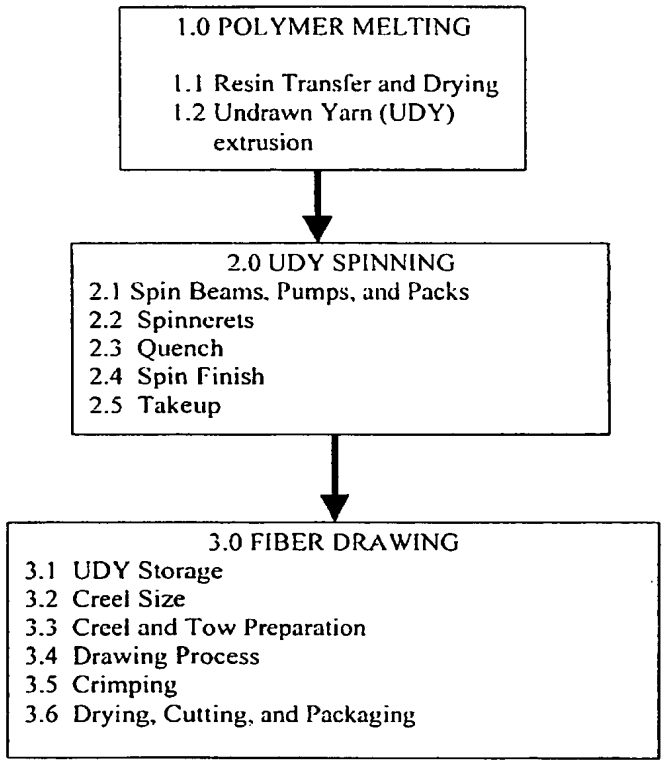
(74) Agent: **HAAS, Donald, F.**; Shell Oil Company, One Shell Plaza, P.O. Box 2463, Houston, TX 77252-2463 (US).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian

[Continued on next page]

(54) Title: POLY(TRIMETHYLENE) TEREPHTHALATE TEXTILE STAPLE PRODUCTION



(57) Abstract: A process for making textile staple fibre from polytrimethylene terephthalate (PTT) which comprises: (a) melt extruding PTT polymer at 245 to 253 °C, (b) spinning the extruded PTT into yarn using at least one spinneret, (c) moving the spun yarn to a first takeup roll wherein the distance from the spinneret to the roll is from 16 to 20 feet, (d) cooling the spun yarn to less than 31 °C before it reaches the roll, (e) prior to the draw process, preconditioning the yarn under tension at a temperature of at least 60 °C, (f) drawing the yarn at a temperature of at least 60 °C, (g) allowing the drawn yarn to relax at a temperature of up to 190 °C, and (h) crimping the drawn yarn at a temperature of 70 to 120 °C, and decreasing the drawn yarn feed denier into the crimper by 10 to 60 percent by denier.

WO 01/68962 A3

patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

INTERNATIONAL SEARCH REPORT

Int .tional Application No
PCT/US 01/08230

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D01F6/62

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 745 711 A (SHELL INT RESEARCH) 4 December 1996 (1996-12-04) claims 1,5,6 ---	1-3,9,10
A	EP 0 949 363 A (COOKSON FIBERS INC) 13 October 1999 (1999-10-13) claims 1,2,6; example 2 ---	1,2,4,9, 10
A	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 06, 22 September 2000 (2000-09-22) & JP 2000 073230 A (UNITIKA LTD), 7 March 2000 (2000-03-07) abstract ---	1,9
A	US 5 645 782 A (HOWELL JAMES MILTON ET AL) 8 July 1997 (1997-07-08) claim 1 -----	1,2,9

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
8 October 2001	15/10/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	D'Souza, J

1

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INTERNATIONAL SEARCH REPORT

Information on patent family members

In: ational Application No
PCT/US 01/08230

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0745711 A	04-12-1996	AU 695724 B2	20-08-1998
		AU 5209096 A	21-11-1996
		BR 9602162 A	30-12-1997
		CA 2175875 A1	09-11-1996
		EP 0745711 A1	04-12-1996
		JP 9003724 A	07-01-1997
		RU 2109861 C1	27-04-1998
		TR 960983 A2	21-11-1996
		TW 389798 B	11-05-2000
		US 6254961 B1	03-07-2001
		US 6113825 A	05-09-2000
EP 0949363 A	13-10-1999	US 6109015 A	29-08-2000
		EP 0949363 A2	13-10-1999
		GB 2336124 A	13-10-1999
JP 2000073230 A	07-03-2000	NONE	
US 5645782 A	08-07-1997	AT 204345 T	15-09-2001
		CA 2189548 A1	11-01-1996
		DE 69522226 D1	20-09-2001
		EP 0767846 A1	16-04-1997
		JP 10502139 T	24-02-1998
		KR 219107 B1	01-10-1999
		WO 9600808 A1	11-01-1996
		US 6242091 B1	05-06-2001
		US 5662980 A	02-09-1997
		US 2001021433 A1	13-09-2001

US 20020071951A1

(19) United States

(12) Patent Application Publication (10) Pub. No.: US 2002/0071951 A1

Hernandez et al. (43) Pub. Date: Jun. 13, 2002

(54) PROCESS FOR MAKING POLY(TRIMETHYLENE TEREPHTHALATE) STAPLE FIBERS, AND POLY(TRIMETHYLENE TEREPHTHALATE) STAPLE FIBERS, YARNS AND FABRICS

(76) Inventors: **Ismael A. Hernandez**, Clemmons, NC (US); **Geoffrey David Hietpas**, Newark, DE (US); **James M. Howell**, Greenville, NC (US); **Claudia Schultze**, Greenville, DE (US)

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LEGAL PATENT RECORDS CENTER
BARLEY MILL PLAZA 25/1128
4417 LANCASTER PIKE
WILMINGTON, DE 19805 (US)

(21) Appl. No.: **09/934,904**

(22) Filed: **Aug. 22, 2001**

Related U.S. Application Data

(63) Non-provisional of provisional application No. 60/231,852, filed on Sep. 12, 2000.

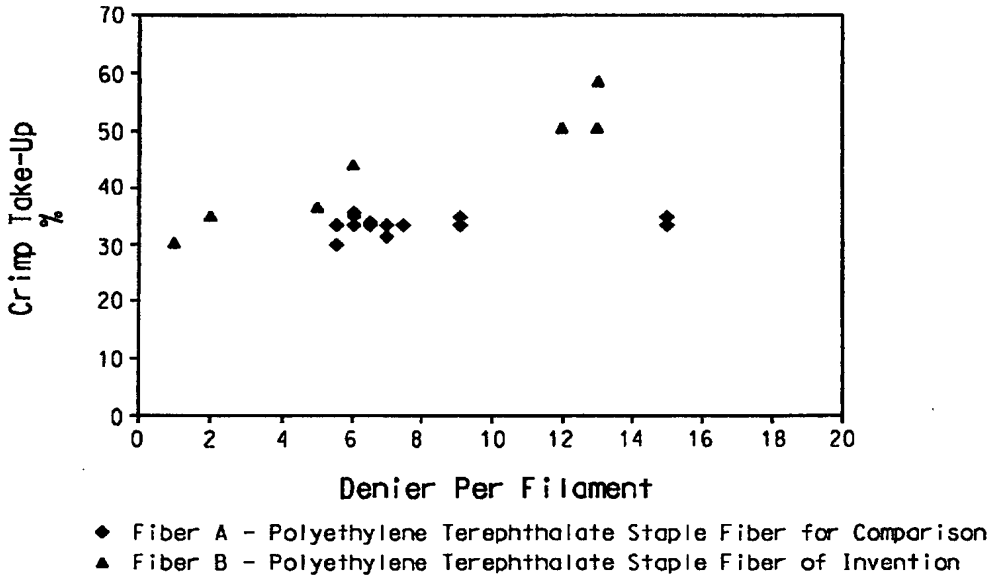
Publication Classification

(51) **Int. Cl.**[7] **D01D 5/088**; D01D 5/26; D01D 10/02; D01F 6/62; D02G 1/00; D02G 3/00

(52) **U.S. Cl.** ..... **428/359**; 264/40.1; 264/143; 264/168; 264/210.5; 264/210.8; 264/211.14; 264/211.17; 264/235; 264/342 RE; 428/364; 428/397

(57) **ABSTRACT**

A process of making polytrimethylene terephthalate staple fibers, comprising (a) providing polytrimethylene terephthalate, (b) melt spinning the melted polytrimethylene terephthalate at a temperature of 245-285° C. into filaments, (c) quenching the filaments, (d) drawing the quenched filaments, (e) crimping the drawn filaments using a mechanical crimper at a crimp level of 8-30 crimps per inch (3-12 crimps/cm), (f) relaxing the crimped filaments at a temperature of 50-120° C., and (g) cutting the relaxed filaments into staple fibers having a length of about 0.2-6 inches (about 0.5-about 15 cm), and polytrimethylene terephthalate staple fibers, yarns and fabrics. Further, a process of optimizing the crimp take-up of a polytrimethylene terephthalate staple fiber comprising determining the relationship between denier and crimp take-up and manufacturing staple fibers having a denier selected based upon that determination.



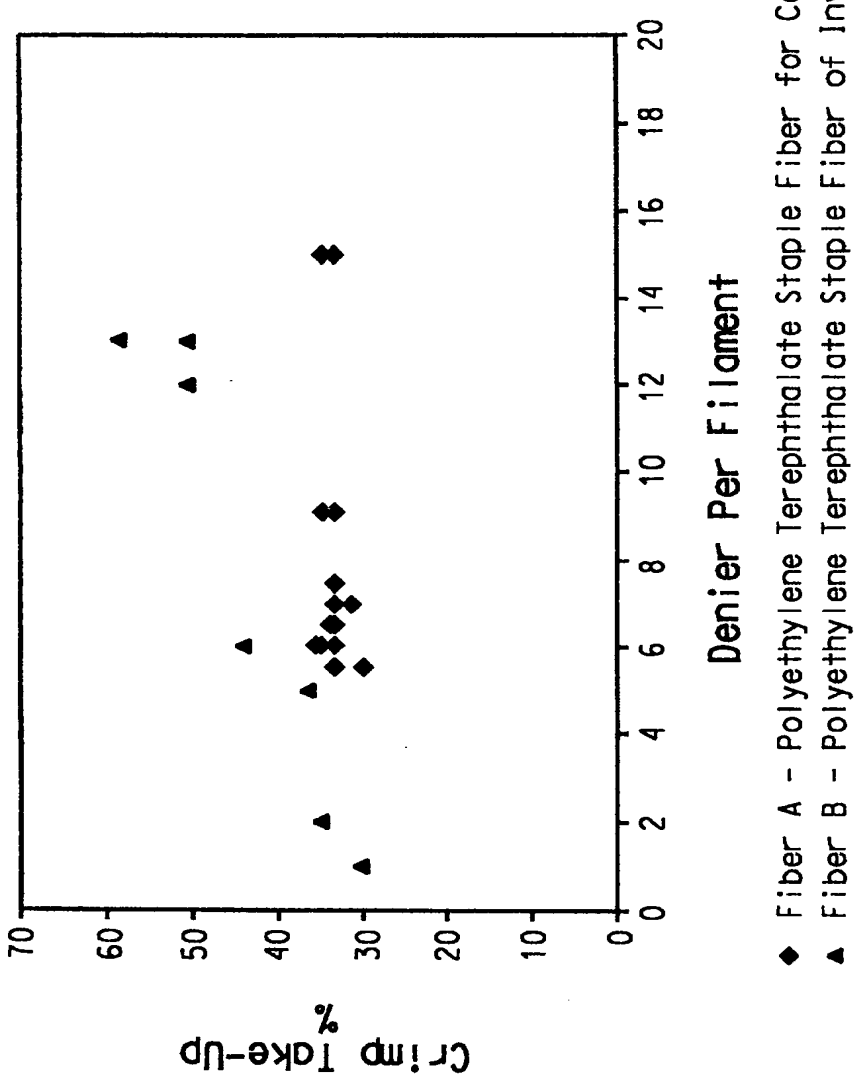

Crimp Take-Up %
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
14
16
18
20
Denier Per Filament
◆ Fiber A - Polyethylene Terephthalate Staple Fiber for Comparison
▲ Fiber B - Polyethylene Terephthalate Staple Fiber of Invention

FIG. 1

PROCESS FOR MAKING POLY(TRIMETHYLENE TEREPHTHALATE) STAPLE FIBERS, AND POLY(TRIMETHYLENE TEREPHTHALATE) STAPLE FIBERS, YARNS AND FABRICS

RELATED APPLICATIONS

[0001] This application claims priority from U.S. Provisional Patent Application Serial No. 60/231,852, filed Sep. 12, 2000, which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The invention relates to a process for making poly(trimethylene terephthalate) ("3GT") crimped staple fibers suitable for yarn and other textile applications, to staple fibers, and to yarns and fabrics made from the staple fibers.

BACKGROUND OF THE INVENTION

[0003] Polyethylene terephthalate ("2GT") and polybutylene terephthalate ("4GT"), generally referred to as "polyalkylene terephthalates", are common commercial polyesters. Polyalkylene terephthalates have excellent physical and chemical properties, in particular chemical, heat and light stability, high melting points and high strength. As a result they have been widely used for resins, films and fibers.

[0004] Polytrimethylene terephthalate ("3GT") has achieved growing commercial interest as a fiber because of the recent developments in lower cost routes to 1,3-propane diol (PDO), one of the polymer backbone monomer components. 3GT has long been desirable in fiber form for its disperse dyeability at atmospheric pressure, low bending modulus, elastic recovery and resilience.

[0005] In many textile end-uses, staple fibers are preferred over continuous filament. These may include staple spun yarns for apparel fabrics, nonwoven materials, and fiberfills and battings. The manufacture of staple fiber suitable for these end uses poses a number of special problems, particularly in obtaining satisfactory fiber crimp, essential for downstream processing such as carding, and in providing a fiber with sufficient toughness (breaking tenacity and abrasion resistance) to produce staple spun yarns with sufficient strength for knitting and weaving for apparel end uses. In the case of 2GT, which is a widely used staple fiber in cotton systems processing as well as in fiberfill and nonwovens applications, these problems are being met by the fiber producers through improvements in polymerization chemistry and optimized fiber production. This has led to improved spinning, drawing and annealing processes tailored to the production of high performance 2GT fibers. There is a need for an improved 3GT staple fiber process which generates fibers with suitable processability in commercial mills employing carding and garnetting processes. The solutions to these problems developed over the years for 2GT or 4GT fibers frequently do not apply to 3GT fibers because of 3GT's unique properties. These needs for tailored fiber properties in a typical 3GT staple yarn spinning process are further described below.

[0006] Downstream processing of staple fibers is typically done on cotton systems equipment. This process includes several steps, many of which are done at high speeds and subject the fibers to a significant amount of abrasion, placing demands on the fiber tensile properties. For example, the initial step is fiber opening, which is often done by tumbling the fibers on motorized belts which contain rows of pointed steel teeth for the purposes of pulling and separating large group of fibers. The opened fibers are then conveyed via forced air and, typically, are then passed thorough networks of overhead ductwork or chute feeders. The chute feeders feed the card, a device which separates the fibers and spreads them into a sheet-like layer, which is then fed into a series of rolls containing combing teeth at high speeds. The carded material is then either processed as a web into nonwoven fabrics or fiberfill applications, or is converted into a sliver for conversion into spun yarns. If converted to a sliver, it is then drawn at high speeds to increase uniformity. The draw process reduces the linear density, defined as weight per unit length, typically by a factor of 5 or 6. The drawn sliver is then spun into a yarn. Staple yarn may be spun from the drawn sliver by a number of commercial methods. These include ring spinning, open-end spinning, air jet spinning, and vortex spinning. All of these methods involve high speed twisting of the fibers, and passage of the yarn under tension over contact surfaces (e.g. guides and eyelets) during wind-up of the final yarn.

[0007] There are two major criteria for acceptable fibers in the above spun yarn process. The first is that the fibers must be suitable for making yarns of a fineness preferred for fabric and apparel applications. Since by definition, a staple yarn is composed of a series of short discontinuous fibers held together solely by twist and fiber-to-fiber friction, a certain minimum number of fibers, typically 100-180 fibers, are required in the cross section of the textile yarn to give it strength and continuity. This has the effect of limiting the range of the fiber denier per filament (dpf), and restricts the practical range of denier useful to make textile yarns to approximately 3 denier per filament and below. There is in principle no lower limit, but the carding process described above does not perform properly below about 0.8 denier per filament, making the overall practical denier range about 0.8 to about 3 denier per filament (about 0.9 to about 3.3 dtex) for spun yarns. Nonwovens typically utilize about 1.5 to about 6 dpf (about 1.65 to about 6.6 dtex) staple fibers. Higher denier fibers may be required for non-textile applications such as fiberfill, which utilize about 0.8 to about 15 dpf (about 0.88 to about 16.5 dtex) staple fibers.

[0008] The second condition is that the fibers must possess a critical set of physical properties to pass through the process with excellent efficiency (minimal fiber damage, nep formation, and various stoppages), while making a yarn, nonwoven fabric, or fiberfill material with sufficient strength for the desired textile end uses. With staple yarns it is especially important they have sufficient strength for knitting and weaving, and sufficient uniformity that they do not cause streaks and unevenness during dyeing and finishing.

[0009] For spun yarns containing synthetic fibers, one of the most critical parameters is fiber strength, defined as tenacity or grams of breaking strength per unit denier. It is particularly important in the case of low denier filaments, such as 1 to 3 denier per filament. In the case of 2GT, fiber tenacities of 4 to 7 grams per denier (gpd) are obtainable with low denier filaments. However, in the case of 3GT, typical tenacities are below 3 grams per denier in the low

denier region. These fibers with only a few grams of breaking strength are not desirable for staple downstream processing.

[0010] There is a need for 3GT staple fibers with tenacities over 3 grams per denier which can be processed into an acceptable staple yarn via spinning techniques such as ring spinning, open end spinning, air jet spinning or vortex spinning. Another important property is the crimp take-up, which is important both for processing the staple fibers and for the properties of textile and fiberfill products made from the staple fibers. The crimp take-up measures the springiness of the fiber as imparted by the mechanical crimping process, and thus affects its handling characteristics such as downstream processing.

[0011] While commercial availability of 3GT is relatively new, research has been conducted for quite some time. For instance, British Patent Specification No. 1 254 826 describes polyalkylene filaments, staple fibers and yarns including 3GT filaments and staple fibers. The focus is on carpet pile and fiberfill. The process of Example 1 was used to make 3GT fibers. It describes passing a filament bundle into a stuffer box crimper, heat setting the crimped product in tow form by subjecting it to temperatures of about 150° C. for a period of 18 minutes, and cutting the heat-set tow into 6 inch staple lengths.

[0012] EP 1 016 741 describes using a phosphorus additive and certain 3GT polymer quality constraints for obtaining improved whiteness, melt stability and spinning stability. The filaments and short fibers prepared after spinning and drawing are heat treated at 90-200° C. This document does not teach a process for making a high tenacity crimped 3GT staple fiber.

[0013] JP 11-107081 describes relaxation of 3GT multifilament yarn unstretched fiber at a temperature below 150° C., preferably 110-150° C., for 0.2-0.8 seconds, preferably 0.3-0.6 seconds, followed by false twisting the multifilament yarn. This document does not teach a process for making a high tenacity crimped 3GT staple fiber.

[0014] JP 11-189938 teaches making 3GT short fibers (3-200 mm), and describes a moist heat treatment step at 100-160° C. for 0.01 to 90 minutes or dry heat treatment step at 100-300° C. for 0.01 to 20 minutes. In Working Example 1, 3GT is spun at 260° C. with a yarn-spinning take-up speed of 1800 m/minute. After drawing the fiber is given a constant length heat treatment at 150° C. for 5 minutes with a liquid bath. Then, it is crimped and cut. Working Example 2 applies a dry heat treatment at 200° C. for 3 minutes to the drawn fibers.

[0015] U.S. Pat. No. 3,584,103 describes a process for melt spinning 3GT filaments having asymmetric birefringence. Helically crimped textile fibers of 3GT are prepared by melt spinning filaments to have asymmetric birefringence across their diameters, drawing the filaments to orient the molecules thereof, annealing the drawn filaments at 100-190° C. while held at constant length, and heating the annealed filaments in a relaxed condition above 45° C., preferably at about 140° C. for 2-10 minutes, to develop crimp. All of the examples demonstrate relaxing the fibers at 140° C.

[0016] All of the documents described above are incorporated herein by reference in their entirety.

[0017] None of these documents teach 3GT staple fibers suitable for textile applications or a process for making them.

SUMMARY OF THE INVENTION

[0018] The invention is directed to a process of making a polytrimethylene terephthalate staple fibers, comprising:

[0019] (a) providing polytrimethylene terephthalate,

[0020] (b) melt spinning the melted polytrimethylene terephthalate at a temperature of 245-285° C. into filaments,

[0021] (c) quenching the filaments,

[0022] (d) drawing the quenched filaments,

[0023] (e) crimping the drawn filaments using a mechanical crimper at a crimp level of 8-30 crimps per inch (3-12 crimps/cm),

[0024] (f) relaxing the crimped filaments at a temperature of 50-120° C., and

[0025] (g) cutting the relaxed filaments into staple fibers having a length of about 0.2-6 inches (about 0.5-about 15 cm).

[0026] The temperature of the relaxation is preferably about 105° C. or below, more preferably about 100° C. or below and most preferably about 80° C. or below. Preferably, the temperature of the relaxation is about 55° C. or above, more preferably about 60° C. or above.

[0027] Preferably, the relaxation is carried out by heating the crimped filaments in an unconstrained condition.

[0028] In one preferred embodiment, the drawn filaments are annealed at 85-115° C. before crimping. Preferably, annealing is carried out under tension using heated rollers. Preferably, the resultant staple fibers have a tenacity of at least 4.0 grams/denier (3.53 cN/dtex) or higher. Preferably, the resultant staple fibers have an elongation of 55% or less.

[0029] Preferably, the staple fibers are 0.8-6 denier per filament. In one preferred embodiment, the staple fibers are 0.8-3 denier per filament.

[0030] The crimp take-up (%) is a function of fiber properties and is preferably 10% or more, more preferably 15% or more, and most preferably 20% or more, and preferably is up to 40%, more preferably up to 60%.

[0031] In another preferred embodiment, the process is carried out without annealing. Preferably, the resultant staple fibers have a tenacity of at least 3.5 grams/denier (3.1 cN/dtex).

[0032] The invention is also directed to a polytrimethylene terephthalate staple fiber of 0.8 to 3 denier per filament having a length of about 0.2 to 6 inches (about 0.5 to about 15 cm), a tenacity of 3.5 grams/denier (3.1 cN/dtex) or more and a crimp take-up of 10-60%, containing 8 to 30 crimps per inch (about 3 to about 12 crimps/cm), prepared without annealing.

[0033] The invention is further directed to a 0.8 to 3 denier per filament polytrimethylene terephthalate staple fiber having a tenacity of 4.0 grams/denier (3.53 cN/dtex) or higher.

Such fibers can have tenacities up to 4.6 grams/denier (4.1 cN/dtex) or higher. Preferably, they have an elongation of 55% or less.

[0034] In addition, the invention is directed to textile yarns and textile or nonwoven fabrics. The described fibers may also be used for fiberfill applications.

[0035] Using the processes of this invention, it is possible to prepare staple fiber and yarn of superior tenacity, softer fabric hand, increased fiber softness, superior moisture transport properties, improved pilling performance and increased stretch and recovery. The preferred fabrics have fuzzy pills (as opposed to hard pills), which results in less pill sensation.

[0036] The invention is also directed to blends of the fibers of the invention and cotton, 2GT, nylon, acrylates, polybutylene terephthalate (4GT) and other fibers. Preferred are yarns, nonwoven, woven and knitted fabrics comprising fibers selected from the group consisting of cotton, polyethylene terephthalate, nylon, acrylate and polybutylene terephthalate fibers.

[0037] The invention is also directed to a process of preparing a polytrimethylene terephthalate staple fiber having a desirable crimp take-up comprising (a) determining the relationship between denier and crimp take-up and (b) manufacturing staple fibers having a denier selected based upon that determination.

DESCRIPTION OF THE DRAWINGS

[0038] **FIG. 1** is a scatter chart showing the relationship between crimp take-up and denier for fibers of the invention and further showing the absence of such relationship in fibers previously known in the art.

DETAILED DESCRIPTION OF THE INVENTION

[0039] The invention is directed to a process for preparing drawn, crimped staple polytrimethylene terephthalate fibers.

[0040] Polytrimethylene terephthalate useful in this invention may be produced by known manufacturing techniques (batch, continuous, etc.), such as described in U.S. Pat. Nos. 5,015,789, 5,276,201, 5,284,979, 5,334,778, 5,364,984, 5,364,987, 5,391,263, 5,434,239, 5,510,454, 5,504,122, 5,532,333, 5,532,404, 5,540,868, 5,633,018, 5,633,362, 5,677,415, 5,686,276, 5,710,315, 5,714,262, 5,730,913, 5,763,104, 5,774,074, 5,786,443, 5,811,496, 5,821,092, 5,830,982, 5,840,957, 5,856,423, 5,962,745, 5,990,265, 6,140,543, 6,245,844, 6,255,442, 6,277,289, 6,281,325 and 6,066,714, EP 998 440, WO 00/58393, 01/09073, 01/09069, 01/34693, 00/14041, 01/14450 and 98/57913, H. L. Traub, "Synthese und textilchemische Eigenschaften des Poly-Trimethyleneterephthalats", Dissertation Universitat Stuttgart (1994), S. Schauhoff, "New Developments in the Production of Polytrimethylene Terephthalate (PTT)", Man-Made Fiber Year Book (September 1996), and U.S. patent Application Ser. Nos. 09/501,700, 09/502,322, 09/502,642 and 09/503,599, all of which are incorporated herein by reference. Polytrimethylene terephthalates useful as the polyester of this invention are commercially available from E. I. du Pont de Nemours and Company, Wilmington, Delaware under the trademark "Sorona".

[0041] The polytrimethylene terephthalate suitable for this invention has an intrinsic viscosity of at 0.60 deciliters/gram (dl/g) or higher, preferably at least 0.70 dl/g, more preferably at least 0.80 dl/g and most preferably at least 0.90 dl/g. The intrinsic viscosity is typically about 1.5 dl/g or less, preferably 1.4 dl/g or less, more preferably 1.2 dl/g or less, and most preferably 1.1 dl/g or less. Polytrimethylene terephthalate homopolymers particularly useful in practicing this invention have a melting point of approximately 225-231° C.

[0042] Spinning can be carried out using conventional techniques and equipment described in the art with respect to polyester fibers, with preferred approaches described herein. For instance, various spinning methods are shown in U.S. Pat. Nos. 3,816,486 and 4,639,347, U.S. patent application Ser. No. 09/855,343, filed May 15, 2001 (Docket No. DP6760), British Patent Specification No. 1 254 826 and JP 11-189938, all of which are incorporated herein by reference.

[0043] The spinning speed is preferably 600 meters per minute or more, and typically 2500 meters per minute or less. The spinning temperature is typically 245° C. or more and 285° C. or less, preferably 275° C. or less. Most preferably the spinning is carried out at about 255° C.

[0044] The spinneret is a conventional spinneret of the type used for conventional polyesters, and hole size, arrangement and number will depend on the desired fiber and spinning equipment.

[0045] Quenching can be carried out in a conventional manner, using air or other fluids described in the art (e.g., nitrogen). Cross-flow, radial or other conventional techniques may be used. Asymmetric quench or other techniques for achieving asymmetric birefringence fibers described in U.S. Pat. No. 3,584,103 (incorporated herein by reference) are not used with this invention.

[0046] Conventional spin finishes are applied after quenching via standard techniques (e.g., using a kiss roll).

[0047] The melt-spun filaments are collected on a tow can. Then, several tow cans are placed together and a large tow is formed from the filaments. After this, the filaments are drawn using conventional techniques, preferably at about 50-about 120 yards/minute (about 46-about 110 m/minute). Draw ratios preferably range from about 1.25-about 4, more preferably from 1.25-2.5. Drawing is preferably carried out using two-stage drawing (see, e.g., U.S. Pat. No. 3,816,486, incorporated herein by reference).

[0048] A finish can be applied during drawing using conventional techniques.

[0049] According to a preferred embodiment, the fibers are annealed after drawing and before crimping and relaxing. By "annealing" is meant that the drawn fibers are heated under tension. Annealing is preferably carried out at least about 85° C., and preferably at about 115° C. or less. Most preferably annealing is carried out at about 100° C. Preferably annealing is carried out using heated rollers. It may also be carried out using saturated steam according to U.S. Pat. No. 4,704,329, which is incorporated herein by reference. According to a second option, annealing is not carried out.

[0050] Conventional mechanical crimping techniques can be used. Preferred is a mechanical staple crimper with a steam assist, such as stuffer box.

[0051] A finish can be applied at the crimper using conventional techniques.

[0052] Crimp level is typically 8 crimps per inch (cpi) (3 crimps per cm (cpc)) or more, preferably 10 cpi (3.9 cpc) or more, and most preferably 14 cpi (5.5 cpc) or more, and typically 30 cpi (11.8 cpc) or less, preferably 25 cpi (9.8 cpc) or less, and more preferably 20 cpi (7.9 cpc) or less. The resulting crimp take-up (%) is a function of fiber properties and is preferably 10% or more, more preferably 15% or more, and most preferably 20% or more, and preferably is up to 40%, more preferably up to 60%.

[0053] The inventors have found that lowering the temperature of the relaxation is critical for obtaining maximum crimp take-up. By "relaxation" is meant that the filaments are heated in an unconstrained condition so that the filaments are free to shrink. Relaxation is carried out after crimping and before cutting. Typically relaxation is carried out to take out shrinkage and dry the fibers. In a typical relaxer, fibers rest on a conveyor belt and pass through an oven. The minimum the temperature of the relaxation useful for this invention is 40° C., as lower temperatures will not permit the fiber to dry in a sufficient amount of time. Relaxation is preferably at a temperature of 120° C. or less, more preferably 105° C. or less, even more preferably at 100° C. or less, still more preferably below 100° C., and most preferably below 80° C. Preferably the temperature of the relaxation is 55° C. or above, more preferably above 55° C., more preferably 60° C. or above, and most preferably above 60° C. Preferably the relaxation time does not exceed about 60 minutes, more preferably it is 25 minutes or less. The relaxation time must be long enough to dry the fibers and bring the fibers to the desired relaxation temperature, which is dependant on the size of the tow denier and can be seconds when small quantities (e.g., 1,000 denier (1,100 dtex)) are relaxed. In commercial settings, times can be as short as 1 minute. Preferably the filaments pass through the oven at a rate of 50-200 yards/minute (46-about 183 meters/minute) for 6-20 minutes or at other rates suitable to relax and dry the fibers.

[0054] Preferably the filaments are collected in a piddler can, followed by cutting and baling. The staple fibers of this invention are preferably cut by a mechanical cutter following relaxation. Preferably, the fibers are about 0.2-about 6 inches (about 0.5-about 15 cm), more preferably about 0.5-about 3 inches (about 1.3-about 7.6 cm), and most preferably about 1.5 inch (3.81 cm). Different staple length may be preferred for different end uses.

[0055] The staple fiber preferably has a tenacity of 3.0 grams/denier (g/d) (2.65 cN/dtex (Conversions to cN/dtex were carried out using 0.883 multiplied by g/d value, which is the industry standard technique.)) or higher, preferably greater than 3.0 g/d (2.65 cN/dtex), to enable processing on high-speed spinning and carding equipment without fiber damage. Staple fibers prepared by drawing and relaxing, but not annealing, have tenacities greater than 3.0 g/d (2.65 cN/dtex), preferably 3.1 g/d (2.74 cN/dtex) or higher. Staple fibers prepared by drawing, relaxing and annealing, have tenacities greater than 3.5 g/d (3.1 cN/dtex), preferably 3.6 g/d (3.2 cN/dtex) or higher, more preferably 3.75 g/d (3.3 cN/dtex) or higher, even more preferably 3.9 g/d (3.44 cN/dtex) or higher, and most preferably 4.0 g/d (3.53 cN/dtex) or higher. Tenacities of up to 6.5 g/d (5.74 cN/dtex) or higher can be prepared by the process of the invention. For some end used, tenacities up to 5 g/d (4.4 cN/dtex), preferably 4.6 g/d (4.1 cN/dtex), are preferred. High tenacities may cause excessive fiber pilling on textile surfaces. Most notably, these tenacities can be achieved with elongations (elongation to break) of 55% or less, and normally 20% or more.

[0056] The fibers prepared according to this invention for apparel (e.g., knitted and woven fabrics) and nonwovens are typically at least 0.8 denier per filament (dpf) (0.88 decitex (dtex)), preferably at least 1 dpf (1.1 dtex), and most preferably at least 1.2 dpf (1.3 dtex). They preferably are 3 dpf (3.3 dtex) or less, more preferably 2.5 dpf (2.8 dtex) or less, and most preferably 2 dpf (2.2 dtex) or less. Most preferred is about 1.4 dpf (about 1.5 dtex). Nonwovens typically utilize about 1.5-about 6 dpf (about 1.65-about 6.6 dtex) staple fibers. Higher denier fibers up to 6 dpf (6.6 dtex) can be used, and even higher deniers are useful for non-textile uses such as fiberfill.

[0057] Fiberfill utilizes about 0.8-about 15 dpf (about 0.88-about 16.5 dtex) staple fibers. The fibers prepared for fiberfill are typically at least 3 dpf (3.3 dtex), more preferably at least 6 dpf (6.6 dtex). They typically are 15 dpf (16.5 dtex) or less, more preferably 9 dpf (9.9 dtex) or less.

[0058] The fibers preferably contain at least 85 weight %, more preferably 90 weight % and even more preferably at least 95 weight % polytrimethylene terephthalate polymer. The most preferred polymers contain substantially all polytrimethylene terephthalate polymer and the additives used in polytrimethylene terephthalate fibers. (Additives include antioxidants, stabilizers (e.g., UV stabilizers), delusterants (e.g., TiO_2, zinc sulfide or zinc oxide), pigments (e.g., TiO_2, etc.), flame retardants, antistats, dyes, fillers (such as calcium carbonate), antimicrobial agents, antistatic agents, optical brightners, extenders, processing aids and other compounds that enhance the manufacturing process or performance of polytrimethylene terephthalate.) When used, TiO_2 is preferably added in an amount of at least about 0.01 weight %, more preferably at least about 0.02 weight %, and preferably up to about 5% weight %, more preferably up to about 3 weight %, and most preferably up to about 2 weight %, by weight of the polymers or fibers. Dull polymers preferably contain about 2 weight % and semi-dull polymers preferably contain about 0.3 weight %.

[0059] The fibers of this invention are monocomponent fibers. (Thus, specifically excluded are bicomponent and multicomponent fibers, such as sheath core or side-by-side fibers made of two different types of polymers or two of the same polymer having different characteristics in each region, but does not exclude other polymers being dispersed in the fiber and additives being present.) They can be solid, hollow or multi-hollow. Round fibers or other shapes can be prepared.

[0060] End uses such as yarns and nonwoven materials are typically prepared by opening the bales, optionally blending them with other staple fibers, and carding them. In making nonwovens, the fibers are bonded by standard methods (e.g., thermal bonding, needelepunching, spunlacing, etc.). In making yarns, the carded material is drawn as sliver and spun into a yarn. Then, the yarn is knitted or woven into fabric.

EXAMPLES

[0061] Measurements and Units

[0062] Measurements discussed herein were made using conventional U.S. textile units, including denier, which is a metric unit. To meet prescriptive practices elsewhere, the U.S. units are reported herein, together with the corresponding metric units in parenthesis.

[0063] Specific properties of the fibers were measured as described below.

[0064] Relative Viscosity

[0065] Relative Viscosity ("LRV") is the viscosity of polymer dissolved in HFIP solvent (hexafluoroisopropanol containing 100 ppm of 98% reagent grade sulfuric acid). The viscosity measuring apparatus is a capillary viscometer obtainable from a number of commercial vendors (Design Scientific, Cannon, etc.). The relative viscosity in centistokes is measured on a 4.75 wt. % solution of polymer in HFIP at 25° C. as compared with the viscosity of pure HFIP at 25° C.

[0066] Intrinsic Viscosity

[0067] The intrinsic viscosity (IV) was determined using viscosity measured with a Viscotek Forced Flow Viscometer Y900 (Viscotek Corporation, Houston, Tex.) for the polyester dissolved in 50/50 weight % trifluoroacetic acid/methylene chloride at a 0.4 grams/dL concentration at 19° C. following an automated method based on ASTM D 5225-92.

[0068] Crimp Take-Up

[0069] One measure of a fiber's resilience is crimp take-up ("CTU") which measures how well the indicated frequency and amplitude of the secondary crimp is set in the fiber. Crimp take-up relates the length of the crimped fiber to the length of the extended fiber and thus it is influenced by crimp amplitude, crimp frequency, and the ability of the crimps to resist deformation. Crimp take-up is calculated from the formula:

$$CTU\ (\%)=[100(L_1-L_2)]/L_1$$

[0070] wherein L_1 represents the extended length (fibers hanging under an added load of 0.13±0.02 grams per denier (0.115±0.018 dN/tex) for a period of 30 seconds) and L_2 represents the crimped length (length of the same fibers hanging under no added weight after resting it for 60 seconds after the first extension).

Comparative Example 1

[0071] This comparative example is based on processing polyethylene terephthalate ("2GT") using typical 2GT conditions. 2GT fibers, 6 denier per filament (6.6 dtex) round hollow fibers, were produced by melt extruding 21.6 LRV flake in a conventional manner at 297° C., through a 144-hole spinneret at about 16 pph (7 kg/h), with a spinning speed of about 748 ypm (684 mpm), applying a finish, and collecting yarns on tubes. The yarns collected on these tubes were combined into a tow and drawn at about 100 ypm (91 mpm) in a conventional manner using two-stage drawing (see, e.g., U.S. Pat. No. 3,816,486) in a mostly water bath (containing dilute finish). The first draw stage stretched the fiber about 1.5 times in a bath at 45° C. A subsequent draw of about 2.2 times was performed in a bath at 98° C. The fiber was then crimped in a conventional manner, using a conventional mechanical staple crimper, with steam assist. The fiber was crimped using two different crimp levels and two different steam levels. The fibers were then relaxed in a conventional manner at 180° C. The crimp take-up ("CTU") was measured after crimping and is listed below in Table 1.

TABLE 1

Effect of 180° C. Relaxation Temperature on 2GT

Crimp Level, Cpi (c/cm)	Steam Pressure, psi (kPa)	Relaxation Temp., ° C.	Crimp Take-Up, %
6 (2)	15 (103)	180	48
10 (4)	15 (103)	180	36
6 (2)	50 (345)	180	38
10 (4)	50 (345)	180	48

Example 1 (Control—High Temperature Relaxer Conditions)

[0072] This example illustrates that when staple fibers are prepared using high relaxation temperatures, staple fibers made from 3GT have significantly poorer quality than 2GT staple fibers. 3GT, 6 denier per filament (6.6 dtex) round hollow fibers, were produced using the same processing conditions as the Comparative Example except that, due to the difference in melting point vs. 2GT, the 3GT fibers were extruded at 265° C. The first draw stage stretched the fibers about 1.2 times. The crimp take-up for the 3GT fibers was measured after crimping and is listed below in Table 2.

TABLE 2

Effect of 180° C. Relaxation Temperature on 3GT

Crimp Level, Cpi (c/cm)	Steam Pressure, psi (kPa)	Relaxation Temp., ° C.	Crimp Take-Up, %
6 (2)	15 (103)	180	13
10 (4)	15 (103)	180	11
6 (2)	50 (345)	180	13
10 (4)	50 (345)	180	14

[0073] Comparing the results shown in Tables 1 and 2, it is readily observed that, under similar staple processing conditions, the 3GT fibers made with the high relaxation temperatures have much lower recovery and mechanical strength than 2GT fibers. These properties are essential for many staple fiber products, making the above 3GT results generally marginal or unsatisfactory.

Comparative Example 2

[0074] This comparative example is based on processing 2GT using the inventive processing conditions for 3GT.

[0075] In this example, 2GT fibers of about 6 denier per filament (6.6 dtex) were spun in a conventional manner at about 92 pph (42 kg/h), at 280° C., using a 363-hole spinneret and about 900 ypm (823 mpm) spinning speed and collected on tubes. The yarns collected on these tubes were combined into a tow and drawn at about 100 ypm (91 mpm) in a conventional manner using two-stage drawing in a mostly water bath. The first draw stage stretched the fiber about 3.6 times in a bath at 40° C. A subsequent draw of about 1.1 times was performed in a bath at 75° C. The fibers were then crimped in a conventional manner, using a con-

ventional mechanical staple crimper, with steam assist. The fibers were crimped to about 12 cpi (5 c/cm), using about 15 psi (103 kPa) of steam. The fibers were then relaxed in a conventional manner at several temperatures. Crimp take-up, measured after crimping, is shown in Table 3.

TABLE 3

Effect of Lower Relaxation Temperatures on 2GT at 12 cpi (5 c/cm)

Steam Pressure, psi (kPa)	Relaxation Temp., ° C.	Crimp Take-Up, %
15 (103)	100	32
15 (103)	130	32
15 (103)	150	29
15 (103)	180	28

[0076] The 2GT shows only a slight decrease in recovery as measured by crimp increased relaxation temperature.

Example 2

[0077] In this example, 3GT fibers, 4.0 denier per filament (4.4 dtex) round fibers, were produced by melt extruding flake in a conventional manner at 265° C., through a 144-hole spinneret at about 14 pph (6 kg/h), with a spinning speed of about 550 pm (503 mpm), applying a finish and collecting the yarns on tubes. These yarns were combined into a tow and drawn at about 100 ypm (91 mpm) in a conventional manner using two-stage drawing in a mostly water bath. The first draw stages stretched the fiber about 3.6 times in a mostly water bath at 45° C. A subsequent draw of about 1.1 times was performed in a bath at either 75° C. or 98° C. The fiber was then crimped in a conventional manner, using a conventional mechanical staple crimper, with steam assist. The fiber was crimped to about 12 cpi (5 c/cm) using about 15 psi (103 kPa) of steam. The fibers were then relaxed in a conventional manner at several temperatures. The crimp take-up was measured after crimping and is listed below in Table 4.

TABLE 4

Effect of Lower Relaxation Temperatures on 3GT at 12 cpi (5 c/cm)

Bath Temp., ° C.	Steam Pressure, psi (kPa)	Relaxation Temp., ° C.	Crimp Take-Up, %
75	15 (103)	100	35
75	15 (103)	130	24
75	15 (103)	150	14
75	15 (103)	180	11
98	15 (103)	100	35
98	15 (103)	130	17
98	15 (103)	150	11
98	15 (103)	180	9

[0078] The recovery properties of 3GT, as measured by crimp take-up and illustrated in Table 4, rapidly decreases with increased relaxation temperature. This behvior is surprisingly different from the behavior of 2GT, which as shown in Table 3, experiences only slight decrease in recovery with increased relaxation temperature. This surprising result was duplicated even when using a bath temperature of 98° C. for the second drawing stage, as shown in Table 4. This example also shows that 3GT fibers made according to the more preferred relaxation temperatures of this invention have superior properties over 2GT fibers.

Example 3

[0079] This example demonstrates another surprising correlation found with the 3GT fibers of the invention: varying the denier of the filaments. 3GT fibers of different denier and cross sections were made in a manner similar to the previous example. The recovery of the fibers, i.e., crimp take-up, was measured with the results listed in Table 5 below. The fibers were treated with a silicone slickener such as described in U.S. Pat. No. 4,725,635, which is incorporated herein by reference, which cures at 170° C. when held for at least 4 minutes once the moisture has been driven from the tow. At 170° C. the crimp take-up of the fiber is very low. To produce slick fibers, the staple was held at 100° C. for 8 hours to cure the silicone slickener finish.

TABLE 5

Effect of Filament Denier on 3GT

Filament Denier (dtex)	Fiber Cross-Section	Crimp Take-Up, %
13.0 (14.4)	Round 1-void	50
13.0 (14.4)	Triangular	58
12.0 (13.3)	Triangular 3-void	50
6.0 (6.7)	Round 1-void	44
4.7 (5.2)	Round Solid	36
1.0 (1.1)	Round Solid	30

[0080] As shown in Table 5, the denier of the filaments has a direct impact on the recovery from extension under a constant load per denier, imparted by the mechanical crimp of the filaments. As denier increases, the recovery, i.e., crimp take-up, increases with it. Similar testing with 2GT showed little impact on recovery with changes in denier. This unexpected result is better illustrated in **FIG. 1**. **FIG. 1** plots crimp take-up versus denier per filament for three different types of fibers. Fiber A is a commercially available 2GT fiber. Fiber B is fiber made according to the invention as detailed in Table 5.

[0081] As can be seen in **FIG. 1**, with the 2GT fibers there is little or no change in recovery as denier per filament increases. On the other hand, with the 3GT fibers of the invention, there is a linear increase in recovery as denier per filament increases.

Example 4

[0082] This example demonstrates the preferred embodiment of the invention for a mid-denier round cross section staple fiber prepared under a series of processing conditions.

[0083] Polytrimethylene terephthalate of intrinsic viscosity (IV) 1.04 was dried over an inert gas heated to 175° C. and then melt spun into an undrawn staple tow through 741 hole spinnerets designed to impart a round cross section. The spin block and transfer line temperatures were maintained at 254° C. At the exit of the spinneret, the threadline was quenched via conventional cross flow air. A spin finish was applied to the quenched tow and it was wound up at 1400 yards/min (1280 meters/min). The undrawn tow collected at this stage was determined to be 5.42 dpf (5.96 dtex) with a 238% elongation to break and having a tenacity of 1.93 g/denier (1.7 cN/dtex). The tow product described above was drawn, optionally annealed, crimped, and relaxed under conditions specified below.

Example 4A

[0084] This tow was processed using a two-stage draw-relax procedure. The tow product was drawn via a two-stage draw process with the total draw ratio between the first and the last rolls set to 2.10. In this two stage process, between 80-90% of the total draw was done at room temperature in the first stage, and then the remaining 10-20% of the draw was done while the fiber was immersed in atmospheric steam set to 90-100° C. The tension of the tow line was continually maintained as the tow was fed into a conventional stuffer box crimper. Atmospheric steam was also applied to the tow band during the crimping process. After crimping, the tow band was relaxed in a conveyer oven heated to 56° C. with a residence time in the oven of 6 minutes. The resulting tow was cut to a staple fiber which had a dpf of 3.17 (3.49 dtex). While the draw ratio was set to 2.10 as described above, the reduction in denier from undrawn tow (5.42 dpf) to final staple form (3.17 dpf) suggests a true process draw ratio of 1.71. The difference is caused by shrinkage and relaxation of the fiber during the crimping and relaxer steps. The elongation to break of the staple material was 87% and the fiber tenacity was 3.22 g/denier (2.84 cN/dtex). The crimp take-up of the fiber was 32% with 10 crimp/inch (3.9 crimp/cm).

Example 4B

[0085] This tow was processed the using a single stage draw-relax procedure. The tow product was processed similar to Example 4A with the following modifications. The draw process was done in a single stage while the fiber was immersed in atmospheric steam at 90-100° C. The resulting staple fiber was determined to be 3.21 dpf (3.53 dtex), with an elongation to break of 88%, and the fiber tenacity was 3.03 g/denier (2.7 cN/dtex). The crimp take-up of the fiber was 32% with 10 crimp/inch (3.9 crimp/cm).

Example 4C

[0086] This tow was processed using a two stage draw-anneal-relax procedure. The tow product was draw processed similar to Example 4A, except that in the second stage of the draw process the atmospheric steam was replaced by a water spray heated to 65° C., and the tow was annealed under tension at 110° C. over a series of heated rolls before entering the crimping stage. The relaxer oven was set to 55° C. The resulting staple fiber was determined to be 3.28 dpf (3.61 dtex), with an elongation to break of 86%, and the fiber tenacity was 3.10 g/denier (2.74 cN/dtex). The crimp take-up of the fiber was 32% with 10 crimp/inch (3.9 crimp/cm).

Example 4D

[0087] This tow was processed using a two stage draw-anneal-relax procedure. The tow product was draw processed similar to Example 4C with the following modifications. The total draw ratio was set to 2.52. The annealing temperature was set to 95° C. and the relaxer oven was set to 65° C. The resulting staple fiber was determined to be 2.62 dpf (2.88 dtex), with an elongation to break of 67%, and the fiber tenacity was 3.90 g/denier (3.44 cN/dtex). The crimp take-up of the fiber was 31% with 13 crimp/inch (5.1 crimp/cm).

Example 5

[0088] This example demonstrates the preferred embodiment of the invention for a low denier round cross section staple fiber.

[0089] Polytrimethylene terephthalate of intrinsic viscosity (IV=1.04) was dried over an inert gas heated to 175° C. and then melt spun into an undrawn staple tow through 900 hole spinnerets designed to impart a round cross section. The spin block and transfer line temperatures were maintained at 254° C. At the exit of the spinneret, the threadline was quenched via conventional cross flow air. A spin finish was applied to the quenched tow and it was wound up at 1600 yards/min (1460 meters/min.). The undrawn tow collected at this stage was determined to be 1.86 dpf (2.05 dtex) with a 161% elongation to break and having a tenacity of 2.42 g/denier (2.14 cN/dtex).

[0090] This tow was processed using a two-stage draw-anneal-relax procedure. The tow product was drawn via a two-stage draw process with the total draw ratio between the first and the last rolls set to 2.39. In this two-stage process, between 80-90% of the total draw was done at room temperature in the first stage, and then the remaining 10-20% of the draw was done while the fiber was immersed in an water spray heated to 65° C. The tow was annealed under tension over a series of hot rolls heated to 95° C. The tension of the tow line was continually maintained as the tow was fed into a conventional stuffer box crimper. Atmospheric steam was applied to the tow band during the crimping process. After crimping, the tow band was relaxed in a conveyer oven heated to 65° C. with a residence time in the oven of 6 minutes. The resulting staple fiber was determined to be 1.12 dpf (1.23 dtex), with an elongation to break of 48%, and the fiber tenacity was 4.17 g/denier (3.7 cN/dtex). The crimp take-up of the fiber was 35% with 14 crimp/inch (5.5 crimp/cm).

Example 6

[0091] This example demonstrates preparation of a non-annealed staple fiber using a single stage draw-relax procedure.

[0092] Polytrimethylene terephthalate of intrinsic viscosity 1.04, containing 0.27% TiO_2, was dried in an inert gas at 140° C. and then melt spun into an undrawn staple tow through 1176 hole spinnerettes designed to impart a round fiber cross section. The spin block and transfer line temperatures were maintained at 254° C. At the exit of the spinnerette, the threadline was quenched via conventional cross flow air. A spin finish was applied to the quenched tow and it was collected at 1400 yards/min. The undrawn tow collected at this stage was determined to be 5.24 dpf (5.76 dtex) with a 311% elongation to break and having a tenacity of 1.57 g/denier (1.39 cN/dtex).

[0093] The tow product was drawn via a single stage draw process with the total draw ratio between the first and the last rolls set to 3.00. The tension of the tow line was continually maintained after drawing, while a water spray at 98° C. was applied to the tow. The tow was then fed into a conventional stuffer box crimper. Atmospheric steam and a dilute fiber finish were applied to the tow band during the crimping process. After crimping, the tow band was relaxed in a conveyer oven heated to 60° C. with a residence time in the

oven of 6 minutes. At the exit of the relaxer oven, additional dilute finish was applied to the fiber and it was then conveyed to a container and cut into staple. The elongation to break of the resulting staple material was 71.5% and the fiber tenacity was 3.74 g/denier (3.30 cN/dtex). The crimp take-up of the fiber was 15 with a crimp/inch of 12.

[0094] The foregoing disclosure of embodiments of the invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise forms disclosed. Many variations and modifications of the embodiments described herein will be obvious to one of ordinary skill in the art in light of the above disclosure. The scope of the invention is to be defined only by the claims appended hereto, and by their equivalents.

We claim:

1. A process of making polytrimethylene terephthalate staple fibers, comprising (a) providing polytrimethylene terephthalate, (b) melt spinning the melted polytrimethylene terephthalate at a temperature of 245-285° C. into filaments, (c) quenching the filaments, (d) drawing the quenched filaments, (e) crimping the drawn filaments using a mechanical crimper at a crimp level of 8-30 crimps per inch (3-12 crimps/cm), (f) relaxing the crimped filaments at a temperature of 50-120° C., and (g) cutting the relaxed filaments into staple fibers having a length of about 0.2-6 inches (about 0.5-about 15 cm).

2. The process of claim 1 wherein the temperature of the relaxation is below about 105° C.

3. The process of claim 1 wherein the temperature of the relaxation is about 55-about 105° C.

4. The process of claim 1 wherein the temperature of the relaxation is about 60-about 1 00C.

5. The process of claim 1 wherein the relaxation is carried out by heating the crimped filaments in an unconstrained condition.

6. The process of claim 1 wherein the drawn filaments are annealed at 85-115° C. before crimping.

7. The process of claim 6 wherein the annealing is carried out under tension using heated rollers.

8. The process of claim 1 wherein the staple fibers are 0.8-6 denier per filament.

9. The process of claim 1 wherein the staple fibers are 0.8-3 denier per filament.

10. The process of claim 9, wherein the drawn filaments are annealed at 85-115° C. before crimping and the staple fibers have a tenacity of at least 4.0 grams/denier (3.53 cN/dtex) or higher.

11. The process of claim 10 wherein the staple fibers have an elongation of 55% or less.

12. The process of claim 1 wherein the process is carried out without annealing and the staple fibers have a tenacity of at least 3.5 grams/denier (3.1 cN/dtex).

13. A polytrimethylene terephthalate staple fiber of 0.8-3 denier per filament having a length of about 0.2-6 inches (about 0.5-about 15 cm), a tenacity of 3.5 grams/denier (3.1 cN/dtex) or more and a crimp take-up of 10-60%, containing 8-30 crimps per inch (about 3-about 12 crimps/cm), prepared by the process of claim 13.

14. A 0.8-3 denier per filament polytrimethylene terephthalate staple fiber having a tenacity of 4.0 grams/denier (3.53 cN/dtex) or higher.

15. A polytrimethylene terephthalate staple fiber as claimed in claim 14 wherein the staple fiber has an elongation of 55% or less.

16. Textile yarn prepared with the fibers of claim 13.

17. Textile yarn prepared with fibers of claim 15.

18. Textile or nonwoven fabric prepared with the fibers of claim 13.

19. Textile or nonwoven fabric prepared with the fibers of claim 15.

20. Textile or nonwoven fabric as claimed in claim 18 further comprising fibers selected from the group consisting of cotton, polyethylene terephthalate, nylon, acrylate and polybutylene terephthalate fibers.

21. A process of preparing a polytrimethylene terephthalate staple fiber having a desirable crimp take-up comprising (a) determining the relationship between denier and crimp take-up and (b) manufacturing staple fibers having a denier selected based upon that determination.

* * * * *

APPENDIX C - RELATED PROCEEDINGS APPENDIX

Application Serial No. 10/733,998

NONE

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